Carbon Emissions from Managed Upland Peat

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Abstract

Upland peat is the world's largest store of soil carbon and one of the most climatically sensitive. Concerns have been raised about the stability of the carbon within these stores and how upland peat will respond to climate change.

Climate change is predicted to increase average, maximum and minimum temperatures and also reduce summer rainfall in the UK. This predicted change in climate is hypothesised to reduce water table depth and increase soil respiration in upland peat causing upland peat to, potentially, turn from a net sink of carbon into a carbon net source.

A range of management practises have been and are being carried out in the UK uplands, often with the view to increase grazing density or increase other commercial animal species such as grouse. This qualifies peat as grazed land under the ratified Kyoto protocol, and any demonstrated increase in carbon storage potential can be used to offset carbon emissions from the UK. Therefore, questions have been raised as to the best management practises for carbon storage potential.

By demonstrating that restoration of water table depths in upland peat will reduce CO_2 emissions sufficiently above the corresponding increase in CH_4 emissions associated with water table rise, carbon stores can be stabilised and the carbon storage rate potentially increased. This thesis reports the results from a study of CO_2, both gaseous and dissolved, and CH_4 fluxes across a differential water table, allowing the results to be analysed both spatially and temporally.

From these results a model was constructed from literature and observations, considering dissolved and gaseous CO_2 as being produced by a single mechanism from within soil processes, where hydrological functions, such as rainfall to determine the endpoint for CO_2.

The model was used to analyse for the lowest level of monitoring that still gives a good estimate of the carbon budget for the field site by using mass balance equations from hydrological literature.

To determine whether the model was valid for higher temperatures and lower water table depths, as predicted for climate change, a series of deep peat cores were sampled from the same site as the spatial and temporal study of CO_2 flux and moved to a warmer and drier site. When CO_2 data, measured from the peat cores, was compared to the spatial and temporal CO_2 fluxes a visual correlation was found between gross CO_2 flux for the two data sets, however upon statistical analysis it was shown that the data sets were incomparable for gross, net and primary productivity fluxes.

Closed chamber measurements of CO_2 flux from the spatial and temporal study were compared to eddy covariance measures of CO_2 flux. It was found that short term (hourly-

daily) were poorly correlated whilst longer term (weekly – monthly) fluxes were better correlated.

By studying a peatland on the boundary of peats temperature tolerance, this study can be applied to other peatlands to proved a model of expected responses to climate change for peat both in the UK and around the world.

Declaration and Copyright

I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any other university. Where relevant, all material which is the work of others has been acknowledged.

Signed

Date

20/02/08

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1. Introduction

In studying large stores of carbon, such as upland peat, it is vital to understand the interactions between different carbon stores, and how these stores are important on a global scale. It is also necessary to understand how small perturbations in the global carbon cycle can have both positive and negative feedback mechanisms, both increasing the amount of carbon taken up, or sequestered, and released from environmentally sensitive carbon sources. These perturbations may, and probably will, have an effect on every aspect of our current lifestyles from the energy we use to the weather, both spatially and temporally.

1.1. Introduction to global carbon cycle

The carbon cycle is one of the most important and intimately linked cycles, linking into other cycles such as the Hydrological and Nitrogen cycles, which affects the amount of water and fertility of plants all over the world. The total amount of carbon on earth is approximately 41950 Pg C (Batjes, 1996), of which soil is the largest terrestrial pool of organic carbon with global estimates ranging from 1115 to 2200 Pg C (Batjes, 1992; Eswan *et al.,* 1995; Sombroek *et al* 1993, Batjes, 1996). Reserves of inorganic carbon stored in soils as carbonates have been estimated to be 780-930 Pg C (Schlesinger 1982). Carbon occurs in two main forms on earth, in either an oxidised or a reduced form. In its oxidised form it is found most commonly as either CO_2, $CaCO_3$, or dissolved carbonate. In its reduced form it is normally found as hydrocarbons, or living matter. There are

three main stores of carbon; terrestrial, atmospheric and oceanic.

1.1.1. Terrestrial stores of carbon

The most diverse store of carbon is terrestrial carbon. This store can be broken down further into many smaller carbon stores. One of the most obvious, and most talked about stores of carbon are forests and rainforests. These stores of carbon occur on almost every continent and most environments. These stores of carbon are important in regulating global water cycles, and the production of oxygen and removal of CO_2 from the atmosphere. The second of these stores of carbon are soils, estimated to store 1500 PgC (Solomon *et al.*, 2007; Batjes 1996; Schlensinger 1997). This store is subdivided into further carbon stores, of which the largest is peat, estimated to store 0.45 Pg of carbon of which 0.009 Pg is stored in the UK (Gorham, 1991). Peat is loosely defined, by Johnson and Dunham, as any soil with an organic content above 50%, and a depth greater than 30cm (Johnson,G.A.L; Dunham, K.C., 1963).

1.1.2. Atmospheric carbon store

The smallest store of carbon is the atmosphere, which has a 2002 carbon concentration value of 0.037 volume percent, or 370ppm concentration (Hulme *et al.*, 2002). This value has increased from a value of 280ppm from pre-industrial times (Gerber, *et al.*, 2003). This value is in a state of constant flux and can vary greatly over a few hundred meters due to respiration and photosynthesis of plants and animals and natural sources of CO_2. The total amount of carbon estimated to be stored in the atmosphere is 760 PgC

(Solomon *et al.*, 2007; Batjes 1996; Schlensinger 1997). It is this store of carbon that is, however, of the greatest concern to mankind as this store of carbon affects the temperature at the surface of the earth, weather patterns, water cycles, and biological activity within soils (Wuebbles *et al.*, 2001). Temperature changes due to CO_2 levels are unevenly spread over the planet's surface, with different environments reacting differently to different environmental changes such as water balance and nutrient availability (Hulme *et al.*, 2002). In the long term, changes in CO_2 levels in the atmosphere will affect sea levels, by changing and reducing terrestrial glacier sizes, this affects the amount of land above sea level (Wuebbles *et al.*, 2001). By increasing atmospheric concentrations of CO_2, and thus affecting global temperatures, increased focus has been placed on large global stores of carbon such as peat, and their response to changing temperatures and weather patterns.

1.1.3. Oceanic carbon stores

Carbon stores in the oceans are estimated to be 39,000 Pg C (Batjes, 1996). Oceans are composed of two different carbon stores, a long-term store and a shorter-term store. The short-term store of carbon is dissolved CO_2 in the upper part of the ocean defined as depths shallower than 1000m (Hwang *et al.*, 2006). This part of the ocean absorbs CO_2 directly from the atmosphere and will be affected by storms and algal blooms which will increase and decrease CO_2 concentrations with temperature and season (Bortkovski, 2006). This upper ocean is also responsible for forming carbonate rocks, such as limestone, in shallow marine environments, and is one of the most important oceanic

mechanisms for very long-term carbon storage (Berelson *et al.*, 2007), indeed carbonate rocks are the largest store of carbon on earth. The lower part of the ocean has a longer turnover period compared to dissolved CO_2 in the upper ocean, and carbon-14 studies have shown that waters in the Atlantic can remain in place for hundreds of years (Sarma *et al.*, 2007). The main form of carbon in this layer is dissolved CO_2 and dead organic matter. Dissolved CO_2 in the upper surface waters of the ocean is carried to depth by oceanic downwellings. Organic matter falls into the lower part of the ocean by a continual rain of organic matter from the upper ocean, including dead algal blooms, and faecal matter (Klass *et al.*, 2002).

1.2. Interaction of the global carbon cycle and the environment

All of the three carbon stores described above are intimately linked to each other and to today's environment. The atmospheric concentration of CO_2 is regulated by the amount of carbon released into the atmosphere by both the oceanic and terrestrial sources of carbon, offset against the amount of carbon sequestered by oceanic and terrestrial sinks. Whether an oceanic or terrestrial environment is a source or sink of carbon is based upon a series of driving controls. The first and most important of these drivers is temperature. Temperature regulates all chemical processes on earth, the greater the temperature the faster the rate of a reaction, and the relationship between temperature and reaction rate is an exponential relationship, not a linear one (Arrhenius 1889). Further, temperature

controls the amount of CO_2 that can dissolve in oceanic waters. The warmer any water the less CO_2 can dissolve in it, but with a faster rate of diffusion from the atmosphere into the oceans.

The amount of carbon taken up by ecological processes for both oceanic and terrestrial sinks depends on other factors. Sun light levels, or to be more precisely photosynthetically active radiation (PAR; a specific wavelength that plants photosynthesis at), is important in regulating the amount of CO_2 removed from the atmosphere by photosynthesis. This process again is regulated by temperature, as chemical processes are involved in photosynthesise during the synthesis of sugars from CO_2. Photosynthetically active radiation is important for carbon uptake by the oceans, as algae and plants within the ocean photosynthesis using PAR, and remove CO_2 directly from the ocean, or from the atmosphere by algal blooms and other surface oceanic plants. Plants also rely on nutrients to aid growth. Nutrients come from either artificial application, such as crop spraying, or natural sources from bacterial fixing of nitrogen into the soil, and weathering of rocks. Oceanic nutrients come from river input into the oceans, submarine black smokers, and decomposition of any organic or inorganic matter containing nutrients which can dissolve into the ocean.

1.3. Increased atmospheric carbon

Increased levels of CO_2 are estimated to raise mean global temperatures by up to 4.5^0C by 2100 (Updegraff *et al.*, 1998). This seemingly small rise in the earth's temperature

will be unevenly distributed over the planet, with some areas becoming warmer and drier, while others become colder and wetter, other environments such as the UK will have a similar average temperature, but with greater extremes of temperature such as hotter drier summers and colder wetter winters (Hulme *et al.*, 2002). In a worst-case scenario, the Antarctic ice caps will melt leading to global sea levels rising by several metres. If this happens many of the worlds major cities, such as London, Tokyo, and New York, will either be submerged by the rising sea levels, or will have to build costly flood defences, which are expensive to build and maintain (Ledoux *et al.*, 2005).

One of the main greenhouse gases portrayed in the media, as having mainly come for anthropogenic sources is CO_2. There are however several natural sources of CO_2, with the main source being the weathering of carbon-rich rocks such as limestone. Calcium carbonate ($CaCO_3$) is weathered by rainfall, which is naturally slightly acidic having dissolved CO_2 within the rainfall as carbonic acid. The greater the concentration of CO_2 in the atmosphere the more acidic the rainwater will be and the greater the amount of carbonate rock will react with the acidic rainfall. Volcanic activity is another large release of natural CO_2, emissions from volcanic action occurring from either active or dormant volcanoes and even at spreading plate margins. Other sources of CO_2 include respiration of all plants and animals, and natural forest fires.

Although CH_4 accounts for a smaller proportion of carbon in the atmosphere it has a greater greenhouse effect, approximately 62 time more effective as a green house gas than CO_2 on a 20 year time scale, and 21-24.5 time more effective on a 100 year time

scale, so proportionally is an important gas to be studied (IPCC 1994; Hargreaves *et al.*, 1998; Schimel *et al.*, 1996). One of the main sources of CH_4 is natural and cultivated wetlands representing approximately 40% of atmospheric CH_4 (IPCC, 1995). Ruminates, such as cows, produce significant amounts of CH_4; other natural sources of CH_4 include termite mounds and the anaerobic decomposition of any organic matter. The amount of CH_4 in the atmosphere has been increasing by about 1% per year (Cao, et al 1998). Methane is oxidised in the atmosphere by the OH· radical; the activation energy for this reaction is provided by the long wavelength emitted by the earth from absorbed radiation from the sun. This oxidation reaction produces CO, CO_2 and water vapour as end member products; all of these gases are themselves important greenhouse gases (Beswick et al 1998).

1.4. Global climate change

Increased concentrations of CO_2 in the atmosphere will increase the average global temperature. This temperature increase will not be spread uniformly across the planet, with far northerly and southerly latitudes experiencing the greatest changes. How will this temperature increase affect the carbon stocks at these latitudes? At these very high latitudes, much of the soil remains frozen, with the upper surface (~1m) becoming active during a few short summer months. With a global temperature increase these soils may remain unfrozen for a larger portion of the year, or even remain unfrozen throughout the year. Very little biological activity occurs in frozen soils, however as soon as the soils unfreeze biological activity will increase exponentially with temperature (Arrhenius

1889, Lloyd *et al.*, 1994). This has the potential to release large amounts of CO_2 into the atmosphere, further compounding the problem of climate change (Johansson *et al.*, 2006). A positive effect of climate change is that unproductive lands may become more productive. This could be by drying the land slightly, ensuring plant roots are not water logged, or by increasing the temperature in cold environments and increasing the efficiency of photosynthesis, meaning more CO_2 taken up (Noordwijk *et al.*, 1998). Increased temperature will also increase the rate of carbon turnover in soils, by increasing biological activity both promoting plant growth and soil respiration. Increased temperatures will also have a negative effect on marginal lands, this time at more equatorial latitudes. Marginal land in warmer climes is often dependant on soil moisture as a rate limiting step for plant production. A small increase in global temperatures could desertify these lands, stopping any carbon uptake and decompose any remaining carbon stocks (Lavee *et al.*, 1998). As plants help to regulate the global water cycle, desertification of any land will decrease the amount of water in that area as vegetation buffers sub-surface temperatures by reflecting sunlight, helping to store water in the subsurface by allowing water vapour to condense, and storing water in plant roots. Loss of this vegetation will increase surface temperature, drying the soil, and losing the ability to store water in the soil. Therefore, the proposed increase of a few degrees will have major implications on the amount of CO_2 put into the atmosphere both by increasing the rate of chemical reactions and by reducing the ability of the oceans to store carbon.

Increasing atmospheric temperature will increase the rate of evaporation drying soils, desertifying marginal soils and increasing production and respiration of permafrost soils.

In the case of peat, this will reduce water table depth and thaw permafrost peats. Reducing water table depth will increase the aerobic zone of soils, which will in turn increase the amount of aerobic decomposition by soil microbes, and increase the amount of carbon released and potentially turn peat from a sink of carbon to a source (Lloyd, 2006). Thawing of permafrost peat may lead to an initial pulse of CO_2 and CH_4 which has been stored in permafrost, unable to escape to the atmosphere because of the frozen soils (Hargreaves *et al.*, 2001). Warmer peat will also increase microbial activity, increasing carbon turnover within the peat and may lead to increased CO_2 and CH_4 released to the atmosphere. A positive side effect of thawing of permafrost peat is the increase in plant production by increasing the growing season, possibly offsetting the amount of CO_2 released by increased microbial activity (Oechel *et al.*, 1998). Increased plant growth may also have another negative effect on the carbon storage potential of peat. Increased plant growth may increase the amount of freely available, or liable, carbon into the subsurface of the peat, stimulate carbon turnover by the soil microbes resulting in increase CO_2 release (Huissteden *et al.*, 2006).

1.5. Political views on climate change and carbon emissions

In 1992 in Rio de Janerio a document was produced at the United Nations Conference on Environment and Development (UNCED), informally known as the Earth Summit. The

aims of this treaty were to reduce global carbon emissions by limiting greenhouse gas emissions. The treaty did not specify specific limits for individual countries, and therefore not legally binding. Within the treaty, there were clauses that allowed the creation of protocols that would set these mandatory levels. Of these protocols, the most significant is the Kyoto Protocol. Countries that sign this protocol are committed to reduce their carbon emission to, on average, 5.2% below 1990 levels. In the UK this level for reduction has been set at 12.5% in greenhouse emissions below 1990 levels by 2008-2012 (Defra, 2002). This protocol did not become legally binding until a representative of each country has signed the document and had it ratified by the respective countries' governments. A total of 163 countries have signed the document and ratified it. These countries combined account for 61.6% of the emissions from countries defined as industrialised countries of which the UK falls within this definition. The Kyoto Protocol came into force on the 16th February 2005 (Boiral, 2006). Notable exceptions to the Protocol are USA and Australia, both of who have signed the protocol but have not ratified the protocol with their respective governments. Indeed the last two US Presidents (representing three terms in office) have not brought the protocol before the government for consideration, as the protocol "would result in serious harm to the economy of the United States" (Byrd-Hagel Resolution S.Res.98).

1.6. Efforts being made to reduce Carbon emissions

As part of the Kyoto Protocol, developed countries have committed to reduce their greenhouse gas emissions towards a target date of 2012. At the sixth conference of Parties to the United Nations Framework Convention on Climate Change (UNFCCC) it was agreed that countries could use carbon sequestration resulting from human induced activities since 1990 on grazed land, crop land re-vegetation, or by forest management to help meet reduction targets by increasing carbon storage potential (Worrall *et al.,* 2003). At the Kyoto conference, it was also agreed that carbon trading would be allowable. If a company outperforms its environmental targets set by the government, then the excess carbon can be sold to companies who are unable to reach the targets set by the government, traded internationally at an agreed price. This carbon trading not only encourages companies to reduce their carbon emissions but also encourages companies to aim to reduce their emissions below their set targets.

By allowing managed land to be used to offset the UK's carbon emissions upland peat can be managed for its carbon potential as large areas of peat have been drained. Draining the peatland involved digging a series of interconnected channels and ditches into the peat. This management practise is called gripping and was proposed to increase the amount and quantity of grasses on the peat to improve grazing. Grazed land is classified as managed under the Kyoto protocol, and thus peat falls under this jurisdiction. Peat has been estimated to be a sink of 0.7 Mt C a^{-1} (Cannell *et al.,* 1999),

and there is potential for this figure to increase if UK upland peat can be restored from drained to a more pristine state potential taking up more carbon, and preserving remaining carbon stores.

1.7. Justification of studying Upland Peat

Peat is the largest store of carbon in the UK, larger than the forests of the UK and France combined. Peat, globally, is estimated to store 0.45 Pg C (Gorham 1991) and UK peat is estimate to comprise 13% of global blanket bog (Lindsay *et al.*, 1988). Peat in the UK is on the southern limit of the occurrence of temperate blanket bog and is much more sensitive than more northerly peat to any changes in climate, such as increases in CO_2 concentrations, or changes in temperature and rainfall than any other environment in the UK. It is therefore proposed that peat in the UK can be used to investigate the effects of increased temperature and reduced rainfall on peat at a more northerly latitude. If it is found that UK peat reacts unexpectedly to climate change then this could provide an 'early warning system' for more northerly peat, both in the UK and globally. If it is found that peat in the UK is, or could be, a net sink of carbon, it can be used to offset the UK's carbon emissions, as most of the peat in the UK has been classified as managed land.

Increased organic carbon in drinking water from upland peat causes water treatment to be more expensive as dissolved organic carbon is difficult to remove and incomplete removal may lead to harmful, carcinogenic by-products (Worrall *et al.*, 2003; Fleck *et al.*,

2004). Furthermore, over 50% of the UK's population obtains its drinking water from peat covered catchments and any changes in the carbon cycle may increase the amount of carbon released. Therefore monitoring of the dissolved proportion of the carbon cycle is just as important as measuring the gaseous fluxes of carbon.

From an ecological perspective, UK peat contains many rare plant and animal species that occur nowhere else in the UK, and increased temperatures may lead to a loss of these species through plant invasion and substrate degradation (Tomassen *et al.,* 2004; Turner *et al.,* 1972). Therefore it is important to understand and preserve these unique environments by managing them from both an ecological and a carbon perspective both which are linked through changes in temperature and hydrology. One of these plant species, occurring only in upland environments and responsible for carbon accumulation, are *Sphagnum* mosses. These are a non-vascular plant that grow in compact, spongy mats in acidic, waterlogged conditions. These waterlogged environments result in slow anaerobic biomass decomposition, allowing thick layers of organic rich soils to accumulate over thousands of years becoming peatlands (Waddington *et al* 2001). The above ground net primary productivity (ANPP) of peatlands is lower than the ANPP of other northern ecosystems, because of saturated conditions and low concentrations of essential nutrients, long-term peatland carbon accumulation rates are roughly 10 times larger than the mean long-term soil carbon accumulation rates for an other upland ecosystem soils (Frolking *et al.* 1998; Schlesinger, 1990).

Currently, upland peat in the UK has been managed to maximise profit made from the

land. Upland peat is used primarily for grouse shooting, and sheep grazing (Mackay *et al.*, 1995), and has been managed to improve grazing density by draining large areas of UK peat with the aim of increasing grass diversity and quantity (Wallage *et al.*, 2006). Peat is also managed to improve grouse numbers by cyclic burning of small areas of peat to provide a mosaic pattern of different maturity levels of heather. Heather is the main staple diet and habitat of grouse, with the grouse preferring to nest in older taller heather, and feed on new shoots provided by the burning cycles at different ages in-between burns (Yallop *et al.*, 2006). However, these management practises, although maximising profit, will affect the carbon balance of a peatland and it is unknown how these management practices will affect this fragile cycle. This leads to the main questions proposed by this thesis, and they are; what are the carbon fluxes for a drained site, both gaseous carbon fluxes and dissolved carbon fluxes. This will answer further questions such as; whether this type of management is beneficial for carbon storage, or whether a different management approach needs to be encouraged amongst landowners.

1.8. Peatland restoration techniques

Peatlands have been mined for agronomic and horticultural purposes. Mining involves removing the surface vegetation and draining the peat (Basiliko, *et al.*, 2007). Historically, peat mining was conducted on a small scale using hand-cutting techniques with the peat blocks dried and often used in domestic heat supply especially in countries such as Ireland, Norway, and Canada (Glatzel, *et al.*, 2006). This type of peat mining was gradually phased out by the 1970's in favour of large scale milling and vacuum removal

of peat (Basiliko, *et al.,* 2007).

Peatland restoration aims to reinitiate self-regulatory mechanisms that will lead back to functional peat accumulating ecosystems (Sottocorola *et al.,* 2007). In peatland restoration there are two objectives. The first is the re-establishment of a typical peatland flora including sphagnum moss. The second is the restoration of hydrological conditions suitable for sphagnum growth by ditch blocking and improving microclimate conditions (Silva *et al.,* 1999, Rochefort, 2000, Sottocorola *et al.,* 2007). These aims may be achieved by either passive or active management. Passive management assumes that the site will restore itself, by wind-seeding bare areas from existing preserved areas, and drainage channels will infill by channel collapse and sediment deposition. Active management is a similar process however, channel filling is done by mechanical means, and a seed mix or plant plugs are spread or planted on the bare peat. These planted areas may be limed or fertilised to promote plant growth and stabilise the peat surface.

In North America peatland restoration has occurred on previously mined peat areas with large areas of bare peat. The peat extraction process does not remove all the peat, but leaves a thick residual layer. Vegetation, from other areas of peatland, is spread onto these bare peat areas and comprises of a mix of sphagna, other byrophytes, vascular plants and a seed bank (Rochefort *et al.,* 2002)

Large areas of the North Pennines was drained during the mid 20th century to promote grass species and the quantity of grasses, thus enabling a greater grazing density

increasing profitability from upland peat. In the past 20 years a link has been formed between these grips and increased carbon losses from the upland peat, and little evidence to support an increase in grass species and grass quantity. This increase quantities of carbon in runoff waters has an increased impact on water treatment both aesthetically and chemically. Therefore, the government introduced a grants system to encourage upland farmers to mechanically block theses drainage channels to reduce carbon emissions and promote wetland plant species.

In the Netherlands large areas have been dredged for fuel from low lying peatlands. This has resulted in an open landscape of turf ponds with narrow baulks of uncut peat in between (Borger, 1992). These floating fen peatlands differ from upland peatlands by having a circum-neutral pH and many rare plant species only found on these types of peatlands. One of the main problems with this type of peatland is acidified waters, containing nitrogen. Restoration on these peatlands focuses on removing the acidic waters from the upper water layer and enhance intrusion of calcium rich surface waters (Dekkar *et al.*, 2005).

Long term mining of peatlands has occur in the Pietzmoor NW Germany. Hand-cutting of peat occurred, on a small scale, from the 16th century until 1960. In total 20-30% of the former mire land was degraded. Restoration efforts began in the 1970 and included closing drainage ditches, cutting birch and pine trees down and allowing sheep to graze to minimise tree growth and establishment. Restoration led to a high water table and allowed cotton grass (*Eriophorum* sp.) and *Sphagnum* sp. to spread (Glatzel *et al.*, 2006).

1.9. Review of different measures and experimental designs on peat.

In justifying whether the management of upland peat is beneficial from a carbon storage perspective different methods have been developed to directly and indirectly measure the amount of carbon being released from peat. Carbon can be lost from peat via two pathways; gaseous carbon exchange, and fluvial carbon loss. Gaseous carbon exchange can be further subdivided into CO_2 exchange and CH_4 exchange. Fluvial carbon loss has several different carbon components; dissolved CO_2, dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC).

1.9.1. Gaseous CO_2 measurements

There are several different methods for measuring CO_2 from the peat surface. The first, and oldest method, is an alkali absorption technique where the peat surface is exposed to a strong alkali, such as NaOH or KOH, and the amount of CO_2 fluxing from the surface reacts with the alkali (Yim *et al.,* 2002). This neutralises a proportion of the alkali, and the amount of CO_2 fluxing from the surface can then be found by measuring the amount of remaining alkali by neutralisation with an acid. The time that the container with the alkali in is in contact with the peat surface, and the surface area covered by the container can then be used to calculate the CO_2 flux from the surface. There is literature evidence

that this method underestimates gross CO_2 by as much as 25% (Schlesinger 1977), and the rate of absorption is affected by temperature if KOH is used as the alkali. This method is, however, the most common method to date for making soil respiration measurements (Yim *et al.*, 2002).

The second method is a closed chamber technique, and like the first method, a chamber is placed on the peat surface, and air from within the chamber is sampled using a syringe through a gas tight seal. The sample is collected in small sample vials with a septum in the lid, which can then be analysed for CO_2 and CH_4 using a gas chromatograph. Yavitt *et al.* (2005), transplanted peat cores from various sites in the USA and Canada, and took CO_2 and CH_4 flux measurements from various depths within the peat. Yavitt *et al.* (2005) found CO_2 fluxes, under anoxic conditions, between 1 and 17.5 $\mu gC\ g^{-1}\ h^{-1}$ and CH_4 fluxes between 0.5 to 2250 $ngC\ g^{-1}\ hr^{-1}$. This study bulked samples before taking measurements and it is unknown what effect this will have had on the structure and microbe community within the peat. There was also no consideration for the gaseous carbon exchange due to plants, or indeed carbon losses due to dissolved CO_2 or DOC and POC. A study by Alm *et al.*, (1999) measured CO_2 fluxes in Finland on a drained peatland using the method described above, and measured average CO_2 fluxes of 5.45 mg $C\ m^{-2}h^{-1}$.

A variation on the syringe sampling method uses an infrared gas analyser (IRGA) where air from the sample chamber is passed into a small reference cell and infrared radiation passed into the cell, with the amount of infrared radiation absorbed by the CO_2 being

proportional to the amount of CO_2 in the small sample cell. If CO_2 concentrations are taken over a time course, the change in CO_2 concentration over the surface area of the sample chamber can be used to calculate the CO_2 flux from the peat surface. This technique can be modified to incorporate an automated system by having an open chamber with a sealing lid attached to a mechanical arm. The drawback of closed chamber techniques is that there is likely to be an edge effect from installing collars into the soil surface. As the collars are installed plant roots are likely to be cut, leading to some of the plants dieing within the collar area, reducing the amount of primary productivity CO_2 flux measured. If a clear chamber is used, this will reduce the amount of PAR entering the chamber, therefore if an external PAR gauge is used this will underestimate the amount of CO_2 taken up by the plants. Chapman *et al.*, (1996) studied the emissions of CO_2 from an organic rich soil near Cathiness, UK. Values of CO_2 flux ranged from 6.8 mgC $m^{-2}h^{-1}$ to 169 mgC m^{-2} h^{-1}. Chapman *et al.* (1996) did not measure primary productivity due to plant response to light levels, or consider fluvial carbon losses. Flanagan *et al.*, (2005) took closed chamber measurements of both respiration and net CO_2 flux. Values of gross CO_2 flux ranged from approximately 0 to 0.29 gC $m^{-2}h^{-1}$ whilst net ecosystem exchange had maximum values of approximately -14 μmol $m^{-2}s^{-1}$ (0.61 gC $m^{-2}h^{-1}$). Again in this study there was no consideration of fluvial carbon.

A third method does not use a chamber at all. This method uses an open path infrared gas analyser (IRGA) using a very fast sampling rate to measure the instantaneous concentration of CO_2. This result, combined with three dimensional wind speed measurements and heat flux measurements, provides a CO_2 flux measurement. This

sampling technique samples larger areas than is possible with a chamber, and can take measurements continuously for several weeks without intervention. The main problems with eddy covariance are that the readings become unreliable during wet weather, and are inappropriate over an inhomogeneous landscape such as a gripped peat or a steep hillside. Lafleur *et al.*, (2005) used an eddy covariance method to measure CO_2 flux from Mer Bleue, Canada. Values for maximum day to day in spring and summer ranged from less than 0.72 $mgCm^{-2}\ h^{-1}$ to 3.24 $mgC\ m^{-2}h^{-1}$. Nieveen *et al.*, (2005) measured the carbon exchange on a drained Dutch agricultural peat soil and found the yearly average of gross CO_2 to be 2.2 $mgC\ m^{-2}h^{-1}$ with maximum and minimum values equal to 0.288 $mgC\ m^{-2}h^{-1}$ and 6.69 $mgC\ m^{-2}h^{-1}$ respectively. When compared to peat in the UK, Dutch peat has been managed for agriculture with none of the native mosses, sedges, and shrubs found on UK peat.

1.9.2. Methane Measurements

Direct CH_4 measures from the surface of a peat are normally taken using a closed chamber technique. This involves placing chambers on the surface of the peat and sampling gasses using a syringe, vial and gas seal, which is the same as the CO_2 sampling method described above. The gas samples are normally analysed using gas chromatography. Bortoluzzi *et al.*, (2006), using the above method, found CH_4 fluxes between 21.96 ±22.6 $\mu gC\ m^{-2}h^{-1}$ and 6.26±4.2 $\mu gC\ m^{-2}h^{-1}$ from an upland site in France, but only measured fluxes during times of high solar irradiance, and did not measure CO_2 fluxes through most winter periods.

Another more modern method for sampling CH_4 from a peat surface is using an eddy covariance method. The concentration of CH_4 is found using a tunable laser diode where the laser intensity will be absorbed relative to the concentration of CH_4 within the sample chamber. This will provide real time measures of CH_4 concentrations, however the technical set up of this system is complex and maintenance is very time consuming. Hargreaves *et al.,* (2005), took campaign measurements of CH_4 from a Finnish mire and found average CH_4 fluxes of 19.89 μgC $m^{-2}h^{-1}$ with values ranging between zero and 1100 ng $m^{-2}s^{-1}$. Fowler *et al.* (1995), measured CH_4 fluxes from Cathiness, UK, over a blanket bog, and measured CH_4 fluxes between 0.84 and 1.44 mgC m^{-2} h^{-1} with an average of 0.18 mgC $m^{-2}h^{-1}$.

1.9.3. Dissolved CO_2 measurements

There are several different literature methods used in determining the excess partial pressure of CO_2 in solution. The three main approaches are: a titration method from which the buffering capacity is measured and the excess CO_2 calculated (Neal 1988); a direct measurement of the CO_2 dissolved in solution using a headspace analysis (Hope *et al.,* 1995); a direct measure of the CO_2 from the stream surface using floating chambers (Billet *et al.,* 2006).

Neal (1988) used a gran acidity method to estimate $EpCO_2$ values for an acid sensitive

spruce forested catchment. This method relies on a titrometric determination of the total buffering capacity of the solution using NaOH. From further sub-sampling and analysis the major ion species were found to be; $H_2CO_3^0$, HCO_3^-, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0$, $Al(OH)_4^-$, AlF^{2+}, AlF_2^+, organic groups, OH^-, and H^+. Using this method $EpCO_2$ values between 2 and 4 times atmospheric pressure were found, and the pH ranged from 4.5 to 7.5.

Dai *et al.,* (1996) used a similar approach to Neal (1998) as detailed above, to calculate the $EpCO_2$ values of a spruce-fir forest catchment. Dai *et al.,* (1996) again used a titration approach to determine the hydrophobic and hydrophilic acids of the solution, the difference in approaches occurs during the calculation of the excess CO_2. Dai *et al.*, (1996) used an acid base approach, which is based on the sum of the cations is equal to the sum of the anions, whilst Neal (1998) is a charge balance approach. Unlike the Neal (1988) approach Dai *et al.,* (1996) included a more detailed organic speciation approach, assuming that the organic groups have three ionic states. However Dai did not include CO_2 speciation in the acid base calculations, and therefore excess partial pressure of CO_2 was not reported.

Worrall *et al* (2005) used a similar method to Neal (1998) for calculating inorganic carbon speciation but then used an iteration process to solve for $EpCO_2$ based on Neal (1998) for an initial estimate of $EpCO_2$ and then compares this to the alkalinity measurements for a catchment. Using total calcium, alkalinity, pH and temperature of the stream water the DIC contents of the stream water can be calculated. The amount of

CO_2 degassed from the system, prior to the stream water sample being collected, was estimated using the Jones and Mulholland (1998a) approach. The rate of CO_2 evasion prior to sampling was estimated using a stagnant two film model (Liss *et al* 1974).

Jones *et al.,* (1998) used a titration method to calculate alkalinity and pH, then using inductively coupled plasma emission spectroscopy analysed for Al, B, Ba, Ca, Fe, Mg, Na, Si and Sr. The contribution of carbonate alkalinity to the total alkalinity was calculated using a computer program called PHREEQ which used an acid base balance to calculate the $EpCO_2$ concentration. Jones *et al.,* (1998) reported excess CO_2 values of between 2.8 to 28 time atmospheric equilibrium.

Hope *et al.,* (1995) used a direct measure of dissolved CO_2 in solution. This method involved a closed chamber into which a sample of river water was introduced. The remaining headspace in the chamber was then flushed with an inert gas, and the solution allowed to equilibrate with the headspace. The headspace was then removed from the chamber and the concentration of CO_2 analyses by a gas chromatography. By knowing a) the volume of the chamber, and b) the volume of river water sample, the amount of CO_2 in the sample could be found and thus the excess CO_2 concentration calculated.

Billett *et al.,* (2006) used floating chamber on the surface of peat stream waters, there was then the direct measurement of the free CO_2 within the chamber by using an IRGA, the IRGA was left attached until an adequate flux reading could be measured. This system also allowed carbon-14 to be measured using zeolite traps for analysis by AMS

radiocarbon dating. Billett *et al.*, (2006) reported flux values between 0.84 – 28.5 mg m^{-2} h^{-1}.

1.9.4. Review of other experimental designs compared to this study

Strack *et al.*, (2007) compared carbon fluxes along a natural peatland microtopographic gradient with a controlled water table depth adjacent to a control site. This study measured the effects of water table reduction over a three year period, but concluded that due to changes in vegetation communities no significance in CO_2 fluxes between the water table controlled site and the control site could be established. Lafluer *et al.*, (2005) used a different approach to solving this problem. An eddy covariance method was used to continually measure CO_2 flux in relation to a series of piezometer wells. From this study it was concluded that there was a weak relationship between water table depth and CO_2 flux. Glatzel *et al.* (2006) linked CO_2 efflux to soil moisture, concluding that water table depths reduced below 40 cm trigger large carbon losses, followed by reduced decomposition rates due to dryness. Silvola *et al.* (1996) found that by lowering water table depth increased CO_2 fluxes and that peat with drainage ditches had a correspondingly higher CO_2 fluxes when compared to pristine peat at the same water table depth and soil temperature. Other studies that have linked CO_2 flux to water table depth include Freeman *et al.*, (2001), with the enzyme latch mechanism, Oechel *et al.*, (2000) with a long term study, hypothesised a peat returning from a source of carbon to a sink of carbon. Whilst other studies have found no relationship between water table depth and CO_2 flux such as Lafleur, *et al.*, (2005) and Nieveen *et al.*, (2005).

This project measures CO_2 and CH_4 fluxes across a short (~10m) transect between a freely drainage channel and a blocked drainage channel (See chapter 2 section 2.3.2 for the field site description) creating a differential water table between the two drainage channels. In this project CO_2 flux was measured over a uniform vegetation community allowing both temporal and spatial changing in water table depth to be considered in relation to CO_2 flux. Lafluer's study site was also a pristine bog without drainage, and a flux tower would be inappropriate in this study because of the size of the footprint measured by the flux tower compared to the grip spacing of the field site. In contrast to Strack's field site, the field site used here has a uniform plant community across the transect.

To the author's knowledge, no literature exists which directly considers dissolved CO_2 and gaseous CO_2 produced by a single mechanism. There are, however, several papers that link dissolved CO_2 to soil processes. Jonsson *et al.*, (2007) measured both dissolved CO_2, and gaseous CO_2 flux using a flux tower, and when comparing the total amount of HCO^- in solution to carbon-13 measurements concluded that the main source of CO_2 in solution must have come from soil respiration. Jones *et al.*, (1987) found that dissolved CO_2 came mainly from ground water. It was found that the CO_2 came from within the soils where levels of CO_2 are elevated due to root and heterotrophic respiration, and that these processes are controlled by factors such as nutrient availability, temperature, organic matter quantity and quality and oxygen. Jones *et al.*, (1998) further suggested that variability in dissolved CO_2 concentrations should reflect differences in soil

respiration in different catchments and could potentially be used to characterise variation in soil metabolic activity. However, no consideration was given to gaseous release of CO_2 and that these two sources of CO_2 may be linked. This study proposes that CO_2 is produced within the aerobic zone of peat and is therefore linked to water table depth, and soil temperature, where rainfall, time since last rainfall, flow within the drainage system, hydraulic conductivity of the peat and other hydrological factors determine whether the CO_2 produced will partition into the atmosphere or soil pore waters and ultimately the drainage system.

Studies of CH_4 across a spatial and temporal transect using a closed chamber method, syringe and vial method can sample a much smaller area in greater detail compared with an eddy covariance method. Other studies to use a closed chamber method to study CH_4 include Bortoluzzi *et al.,* 2006 who used a closed chamber method to sample CH_4 on a bog in the Jura Mountains, France. This bog had previously been drained due to peat extraction for horticulture, which ceased in 1984 and spontaneous regeneration started to occur in 1986. Changes in water table depth were only measured temporally as the water table depth was constant across the site. Nankano *et al.,* (2000) used a closed chamber method to measure CH_4 emissions from an artic tundra site, and concluded that CH_4 was related to water table as dry sites released comparably less CH_4 then the wet sites with average emission from two water logged sites being 1.45 mgC m^{-2} h^{-1} and 8.78 mgC $m^{-2}h^{-1}$ whilst emissions from the dry site was near zero. MacDonald *et al.,* (1998), used a closed chamber method to sample methane from a series of peat monoliths, observing CH_4 emissions of 2.11 mgC $m^{-2}h^{-1}$ from a pooled area.

Lloyd (2006) linked water table depth and soil temperature to gross CO_2 flux however did not measure the effects of increased temperature on peat, and assumed that the model held for higher temperatures and lower water table depths. Lloyd (2006) did not consider the contribution of dissolved CO_2 to the overall CO_2 export from the site. In this study closed chamber measurements of gross, and net CO_2 flux from an upland peat were compared to a series of CO_2 flux measurements made on a set of deep peat cores from the same upland field site. The cores were moved to relatively warmer and drier location due to altitude and a rain shadow effect, simulating climate change. The measurements of CO_2 flux from the upland peat were considered in relation to dissolved CO_2 measurements, whilst no dissolved CO_2 was allowed to escape from the peat cores.

From a literature review it has been established that temperature, either air or soil, sunlight (PAR), water table depth, all affect gross and primary productivity fluxes (Lloyd *et al.*, 1994; Nykanen *et al.*, 2003; Lloyd, 2006). From the literature a series of equations linking gross and primary productivity fluxes to the drivers listed above were found (Lloyd *et al.*, 1994; Bubier *et al.*, 1994; Nykanen *et al.*, 2003; Lloyd, 2006). This study reviews these driving variables and the equations used and tries to improve them to account for a greater proportion of the variance within CO_2 (both gross and net) flux data.

This thesis takes mass balance equations from hydrological literature and applies them to dissolved CO_2 and gaseous CO_2 fluxes to obtain the best estimate of a CO_2 budget for the field site and the level of monitoring needed to obtain this estimate. Worrall *et al.*,

(2003) used the same equations to model the export of DOC from upland peat.

Using the CO_2 values measured by the eddy covariance method and comparing the values to closed chamber measurements of CO_2 flux should show how comparable these two types of measurements are. By comparing these two types of results it should be possible to apply corrections to closed chamber measurements to compensate for diurnal variations in the data. Laine *et al.*, (2006) took a similar approach in comparing eddy covariance measurements of net ecosystem exchange with closed chamber methods. This method measured CO_2 fluxes over a year and compared them to weekly and biweekly closed chamber measurements made within the footprint of the flux tower. Laine *et al.*, (2006) found that the comparison between eddy covariance measurements and closed chamber was in poor relationship on short (30 minutes to a day) time scales but on a monthly to annual scale the relationship was very similar, thus concluding that both methods were accurate and valid in measuring CO_2 flux.

From this review of the other experiments, a series of aims can now be established, building on previous work, to incorporate a more complete understanding of the carbon cycle for upland peat into a model that completes both dissolved and gaseous carbon cycle for a managed upland peat.

1.10. Aims

The overall aims of this thesis can be summarised into the following bullet points

- ❖ To determine whether restoration of water table depth can reduce CO_2 emissions both spatially and temporally
- ❖ To find whether dissolved CO_2 has the same source of production as gaseous CO_2 where different drivers determine endpoint
- ❖ To establish what effect water table restoration has on CH_4 flux
- ❖ What effect will increased temperature and reduced water table depth have on gaseous emissions of CO_2
- ❖ Measure and compare CO_2 and CH_4 fluxes measured by eddy covariance with closed chamber measurements
- ❖ Establish the driving variables of gaseous CO_2 flux and combine this with an intensively measured dataset to complete a gaseous carbon budget for the field site
- ❖ Determine the best estimate of the overall carbon budget for the field site, using all available data both measured and modelled and determine the best monitoring level needed to establish such an estimate.

2. Gaseous fluxes

2.1. Introduction

This chapter measures different carbon gases (CO_2 and CH_4) from a restored upland peat. From these measurements of CO_2 and CH_4, the carbon budget for the field site is estimated from relationships to treatment and climatic variables.

2.1.1. Efforts for reducing CO_2 and CH_4 in the atmosphere

The UK is already committed, in agreement with the ratified Kyoto Protocol, to reduce its emissions of CO_2 to 5% below 1990 levels by 2008 – 2012 (Patenaude *et al.*, 2005). To achieve this, the Government must find and implement ways of reducing carbon emissions from industry and ways to mitigate carbon emissions by enhancing environmental carbon sinks. For example, if areas of managed land are found to function as CO_2 sinks then this can be offset against the UK's overall CO_2 release budget.

2.1.2. Effect of drainage on CO_2 and CH_4 fluxes on upland peat

A great deal of interest has been focused on the management of different stores of

terrestrial carbon including peatlands (Garnett *et al.*, 2001). In particular, restoration and maintenance of a near-surface water table depth as a result of 'grip-blocking' has the potential to reduce CO_2 fluxes from the peat surface but how much of the variability of CO_2 fluxes that can be accounted for by changes in water table depth is uncertain (Lafluer *et al.*, 2005, Hasimoto *et al.*, 2006, Oechel *et al.*, 2000). Researchers have also found that seasonal differences in climatic conditions also have a significant effect on both CO_2 and CH_4 fluxes. Nieveen *et al.*, (1998), found, using an eddy covariance method, that there was a distinct seasonal trend to CO_2 flux over a former raised bog, where the bog acted as a sink of carbon during the summer months, and a source of carbon during the winter months, and overall was a net source of 97 gC $m^{-2}a^{-1}$. Yuste *et al.*, (2004), found that there was a power law relationship between the seasonal flux of CO_2 and temperature with greater soil respiration values at higher temperatures. This was expressed by a biological function called Q_{10} which is the ratio of the rate of a reaction occurring at any temperature and the same reaction occurring 10 degrees lower. It was also found that there was a difference in Q_{10} values, soil respiration rates, and vegetation type. Wythers *et al.*, (2005), used a scaling Q_{10} value to model soil respiration values, with respect to changes in season and temperature. Siegal *et al.*, (1995), show a relationship between soil pore water flow and changes in seasonal temperature and rainfall patterns, showing that peat is sensitive to long term (3-5 year) droughts, which will affect water chemistry and CO_2 production rates. Subke *et al.*, (2003), found that 72% of the variance in soil respiration measurements could be accounted for by changes in soil temperature, and a further 11% could be explained by changes in soil moisture. Lloyd *et al.*, (1998), studied the CO_2 release from a high latitude peat site, and found a

seasonal link to temperature, soil moisture, vegetation type, and sunlight levels. Chapman *et al.*, (1996), found a strong relationship between soil temperature and CO_2 flux and predicted that for a climate change increase of 2.5°C there would be an increase of CO_2 flux between 36-59%, and for a 4.5°C increase CO_2 flux was predicted to double. Waddington *et al.*, (2001), studied CO_2 production from a natural and harvested peat, and found that temperature was important in CO_2 production. There was a difference in substrate type depending on whether the samples were taken from a pristine peat, and old block cut peat or a young block cut peat with the old block cut peat having the smallest carbon release and the pristine having the greatest carbon release. With values ranging between 1.25 gμC $g^{-1}h^{-1}$ and 0.2 μgC $g^{-1}h^{-1}$.

The complete carbon budget from a peatland can be summarised by Worrall *et al* (2003).

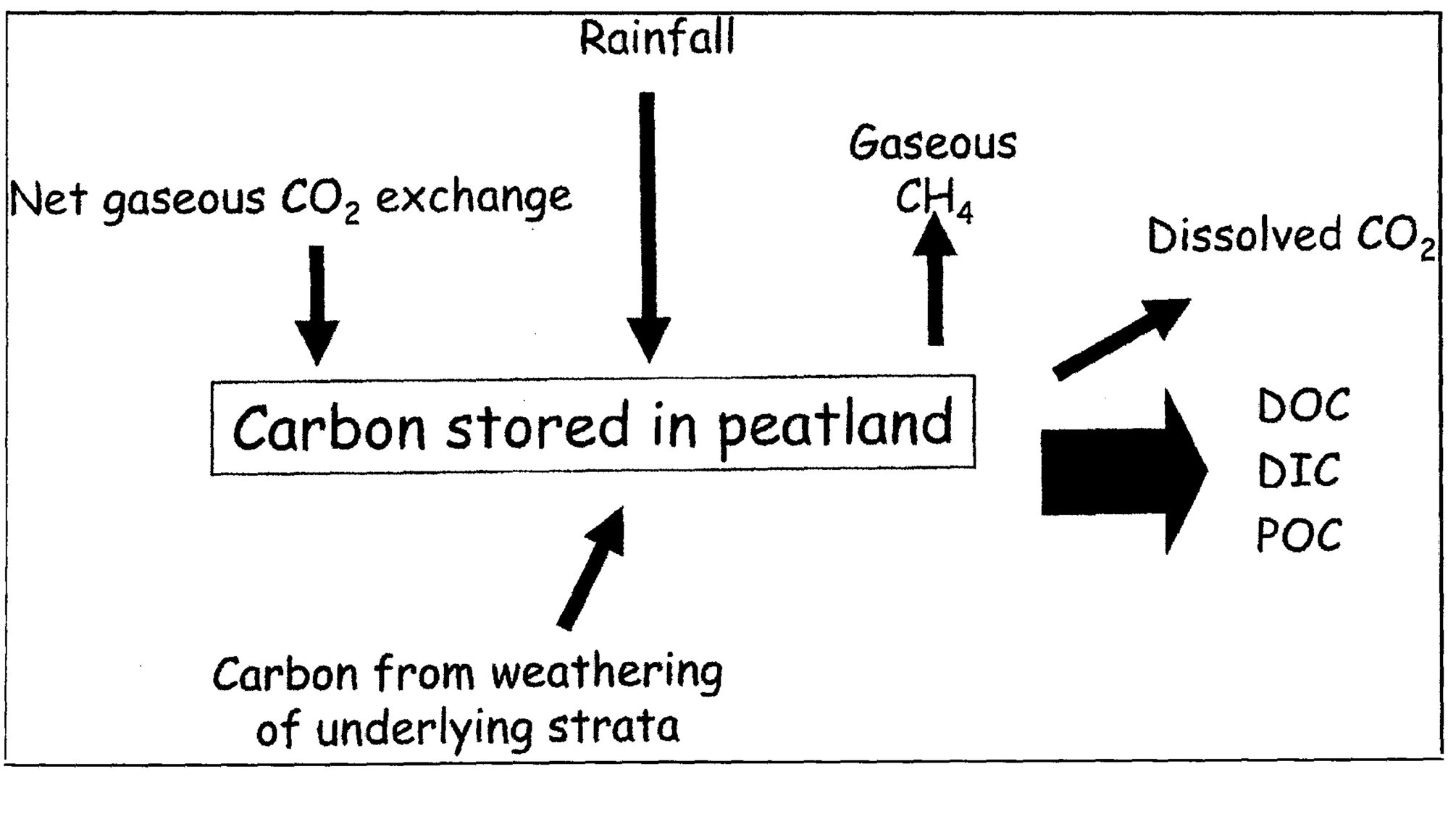

Figure 2.1 Carbon exchange from an upland peat (Worrall *et al.* 2003)

The above diagram (Figure 2.1) shows the different pathways via which carbon may be

lost and the relative magnitude of the losses. Peatlands are hypothesised to be a net sink of gaseous CO_2 based on long-term accumulation rates taken from peat cores (Yu, 2006). Whilst CH_4 is hypothesised to be a small net loss of carbon from the system (Bortoluzzi *et al.,* 2006), this has global implications as CH_4 is 21-24.6 times more effective as a greenhouse gas based on a 100-year timescale (IPCC 1994; Hargreaves *et al.,* 1998; Schimel *et al.,* 1996).

2.2. Objectives and hypothesis

The objectives of this chapter are:-

1. Determine the effect of water table restoration on CO_2 and CH_4 fluxes.
2. To examine the effects of seasonal climate variation on CO_2 and CH_4 fluxes
3. To determine whether season or treatment accounts for most of the variation in CO_2 flux.
4. To calculate the gaseous carbon budget for a restored peat

2.3. Methods

2.3.1. Approach

This section introduces the field site location, and the vegetation classification of the field site. This section goes on to describe the experimental set up and implementation of monitoring. The methods used for the measurements of CO_2 and CH_4 are described, as

well as the theory behind the measurements made. The penultimate methods section describes the climatic measurements made, as well as the instruments used. Finally, this section describes the statistical analyses performed on the data.

2.3.2. Field Site Description

Hexhamshire Common is located 25 miles east of Durham City on the North Pennines. The deep (1m+) ombrotrophic peat bog was intensively drained in 1995 by a process called gripping, with grip spacing's between 7-10m. These drainage ditches were then blocked using a cut-and-shut method approximately every 20m, in January/February of 2003 apart from one drainage ditch, which was left open.

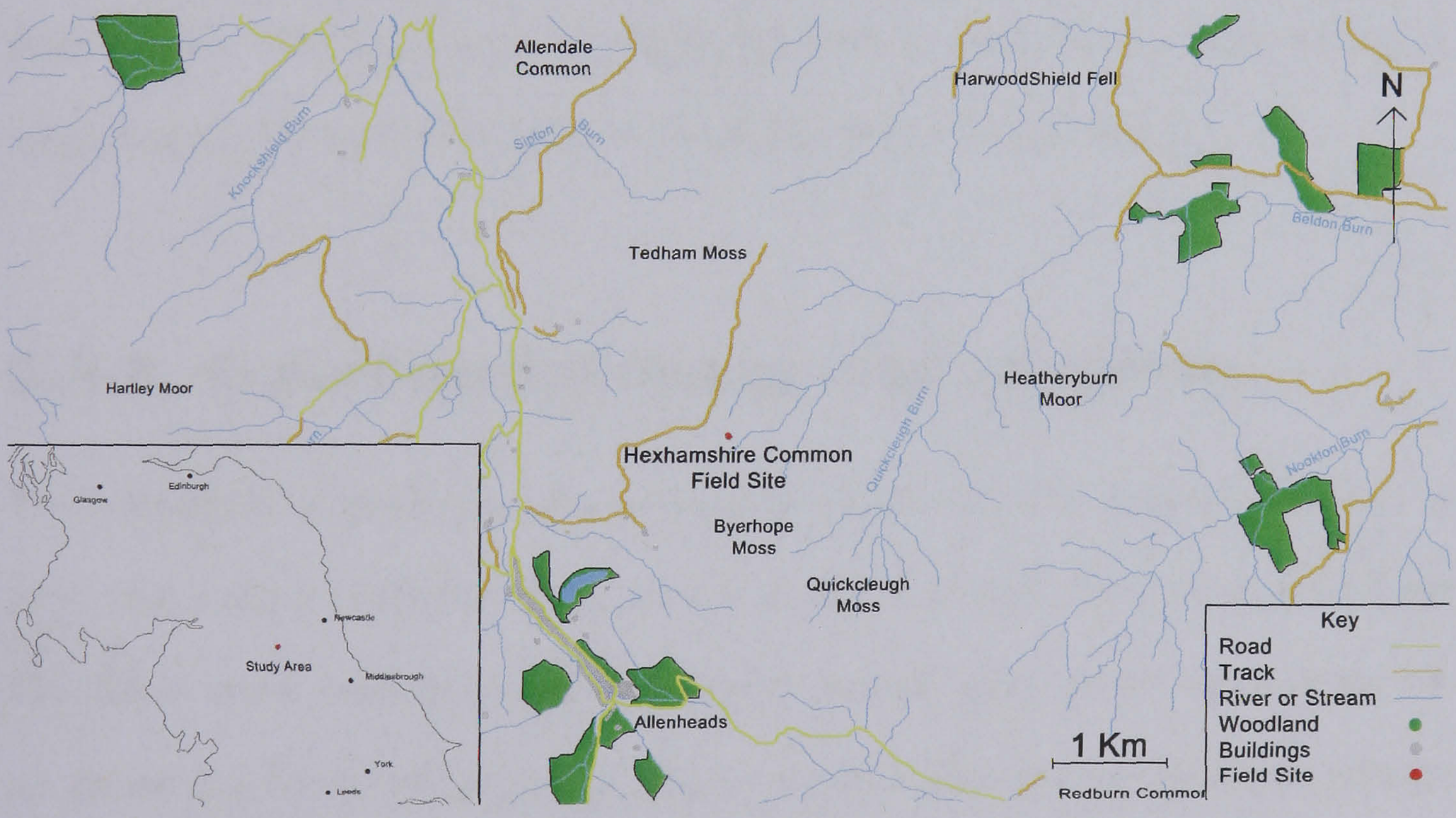

Figure 2.2 Hexhamshire Common field site location map

The Hexhamshire Common field site has been classified according to the National Vegetation Classification (NVC), as an M19 *Calluna vulgaris – Eriophorum vaginatum*

blanket mire. The main plant species are *Sphagnum capillifolium*, *Sphagnum papillosum*, *Polytrichum commune*, *Eriophorum vaginatium* and *Calluna vulgaris*, with infrequent *Pleurozium schriberi*, *Hypnum jutlandium*, *Erica tetralix*, *Rubus chamaemorus*, and *Drosera capillaris*. The proportion of *Calluna vulgaris* has been increased due to burning.

The Hexhamshire Common field site has an altitude of 517m above sea level. The underlying geology of the field site is Carboniferous Millstone Grit, with no apparent glacial deposits. The site is managed on a fifteen year burn cycle, where the whole common has been divided into a series of small (~20m^2) sections. These sections are then grouped together so that the rotation of burning leaves older patches next to newly burnt patches. This encourages a red grouse habitat as grouse nest in older patches in longer heather, but feed in the newly burnt patches on new heather shoots.

2.3.3. Experimental design and sampling

The field site is an intensively and extensively drained site with drainage channels, or grips, dug every 7-10meters. There are two potential methods for measuring CO_2 and CH_4 fluxes at the field site; an eddy covariance method and a closed chamber method. As the site was intensively gripped an eddy covariance method would be inappropriate to measure the CO_2 and CH_4 fluxes because eddy covariance methods require a large and homogeneous surface over which to measure flux and by the very nature of gripping this is no longer the case. To try to find any relationship between water table depth and CO_2

or CH_4 flux a better method would be to use a chamber method where a small area of peat (<1m) can be measured and several replicates and be taken across a differential water table depth. The gaseous fluxes measured from the field site are; gross flux, and net flux. Gross flux is the total CO_2 released from microbial and plant root respiration. Gross CO_2 flux is measured using a covered closed chamber on the peat surface. Net flux is the balance of CO_2 released from gross flux and the total amount of carbon taken up by plants. Net CO_2 flux is measured using a clear closed chamber on the surface of the peat. From these two flux readings (Gross CO_2 flux and Net CO_2 flux) the total amount of CO_2 taken up by the plants can be calculated.

2.3.4. Completing the gaseous carbon budget

Completing the gaseous carbon budget for the site will require measurements of gaseous CO_2 and CH_4 and a relationship to driver variables as defined in the literature as temperature, PAR and water table depth (Lloyd *et al.*, 1994, Nykänen *et al.*, 2003, Bubier *et al.*, Christensen *et al.*, 1996, Hughes *et al.*, 1999). These driver variables will then be used to predict the CO_2 and CH_4 fluxes from the site at a sub-hourly time scale to complete the carbon budget.

The fluxes measured were divided between; CH_4 and CO_2 fluxes, light and dark readings, transect and spatially measured fluxes. Fluxes measured in sunlight are called Net Ecosystem Exchange (NEE) which is the difference between the total amount of CO_2 released by respiration (R), and the total amount of CO_2 taken up by the plants, called

primary productivity (PP). Fluxes measured in the dark, or under a cover, are called gross fluxes, or respiration (R), and is a measure of the total amount of CO_2 released. Carbon dioxide release is positive and CO_2 taken up is negative, in accordance with standard micrometeorological measurements.

Permanently fixed collars, inserted 5 cm's into the peat, for the measurement of CO_2 and CH_4, were divided into 2 groups and comprise of 3 sections in total. The first group and first section formed part of the spatial comparison data set where three pairs of permanently installed collars were grouped between two drainage ditches; one blocked, one unblocked, which forms a transect with a differential water table between the grips (Figure 2.5).

Figure 2.3 Permanently installed collars either side of a piezometer well

Figure 2.4 Example of drain blocked by a peat dam, water flow is from right to left with the peat dam on the left hand side of the picture.

This paring of collars allowed both gross CO_2 flux and net CO_2 flux readings to be taken almost simultaneously. The distance between each of the collar pairs was approximately 3 meters apart. The collars were labelled from the unblocked grip to the blocked grip, measurements of net CO_2 flux were labelled 1 and measurements of gross CO_2 flux were labelled 2, and between the blocked and unblocked labelled a to c. For example the collar closest the unblocked grip and measuring gross CO_2 flux was labelled 2b. The collar closest to the blocked grip measuring net CO_2 flux was labelled 1c (Figure 2.5).

This section of collars was used in conjunction with the last section of the field site (see below and Figure 2.5). From these collars objectives 2 and 4 from section 2.2; determining the effects of season on CO_2 fluxes, and calculating of the carbon budget for

the site, can be answered.

The second group and second section of collars are the main group of collars located across the middle of the site section (Figure 2.5). Across this part of the site, eight collars were installed, again in four pairs, and each paired collar had a piezometer well with a pressure transducer continuously measuring the depth of the water table using a manually calibrated pressure transducer and a data logger (See Figure 2.3). The paired collars were spaced approximately 2.5m from another paired collar set, and the collar pairs were spaced approximately 5 - 10 centimetres apart. The collars were labelled 1 to 8 the odd numbers measured net CO_2 flux and the even numbers measured gross CO_2 flux (Figure 2.5). This collar layout was designed to answer objectives 1, 2, 3, and 4 from section 2.2, with collars 1a to 4b used to answer objectives 2 and 4.

The third section, which is part of the first group, was the second half of the spatial collar data group, again paired collars allowed both gross and net CO_2 fluxes to be measured. Again like the first section of the field site the paired collars were 1.5 meters apart, and the space between the collar pairs was approximately 3 meters apart. The collars were labelled 3 and 4 for net CO_2 flux and gross CO_2 flux respectively.

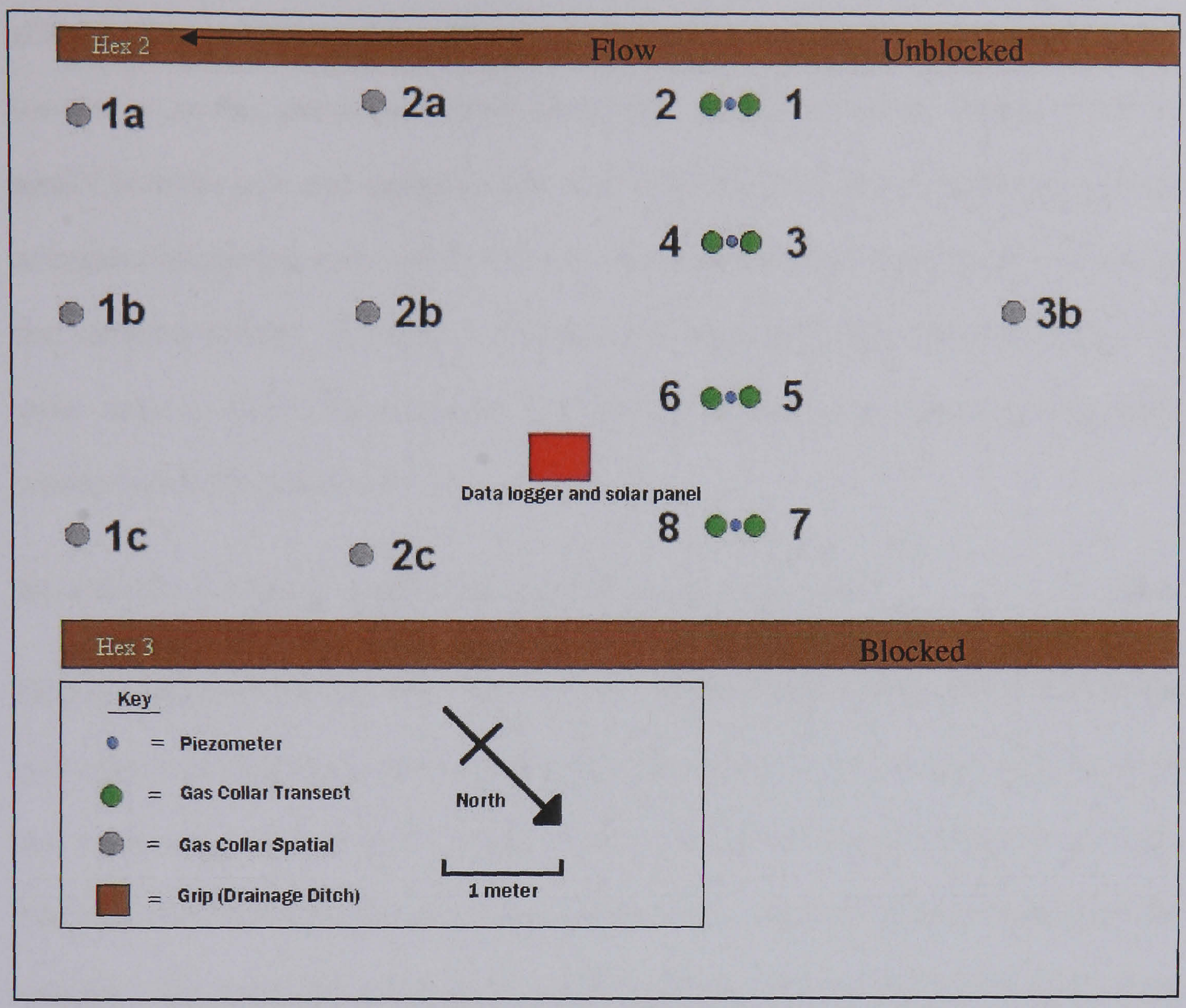

Figure 2.5 Field site layout with collar numbers referred to in the text

2.3.5. Gas flux measurements (CO_2 and CH_4)

There were three types of fluxes; gross, net, and primary productivity fluxes. Gross fluxes are defined as the total amount of CO_2 released from the peat surface in $gCO_2\ m^{-2}h^{-1}$, and CO_2 release is always positive. Primary productivity fluxes are defined as the total amount of CO_2 taken up by the plants on the peat surface, again the units are in

$gCO_2\ m^{-2}\ h^{-1}$, and CO_2 uptake is always negative. Net fluxes are defined as the difference between gross flux and primary productivity flux, and are the overall carbon release or uptake from the peat, and again have the units of $gCO_2\ m^{-2}h^{-1}$, and will either be positive or negative depending upon whether the peat is a source or sink of gaseous carbon during that sampling period. In reality, it is hard to measure primary productivity fluxes, so gross and net fluxes are measured and primary productivity calculated from these measurements (See equation 2.i).

$$\textit{Net } CO_2 \textit{ flux} = \textit{Primary Productivity } CO_2 \textit{ flux} + \textit{gross } CO_2 \textit{ flux} \qquad \textbf{2.i}$$

Measurements of CO_2 flux were collected on a weekly basis during winter months and every three weeks during summer and when grouse chicks were in their fledging stage due to the landowners wishes. Samples were collected, between the 12th of December 2003 and the 22nd of April 2004, on a weekly basis. After the 22nd of April 2004 the samples were collected every three weeks until the 15th of September 2004 when sampling returned to weekly sampling. Measurements for CH_4 calculation were collected on a campaign basis every 3 to 4 months. Campaign of measurements of CH_4 were collected during the same sampling period as the CO_2 fluxes, and started on 22/04/2004 and ran until 10/05/2005.

Carbon Dioxide (CO_2) was measured using two methods. The first method involved using a portable infra-red gas analyser (IRGA) (PP systems EGM-4, Hitchin, UK.) This IRGA was bought with a purpose built clear acrylic closed chamber from PP-systems (PP-systems CPY-2 Canopy Assimilation Chamber, Hitchin, UK), with a perforated

copper manifold which ran around the base of the chamber (Figure 2.6)

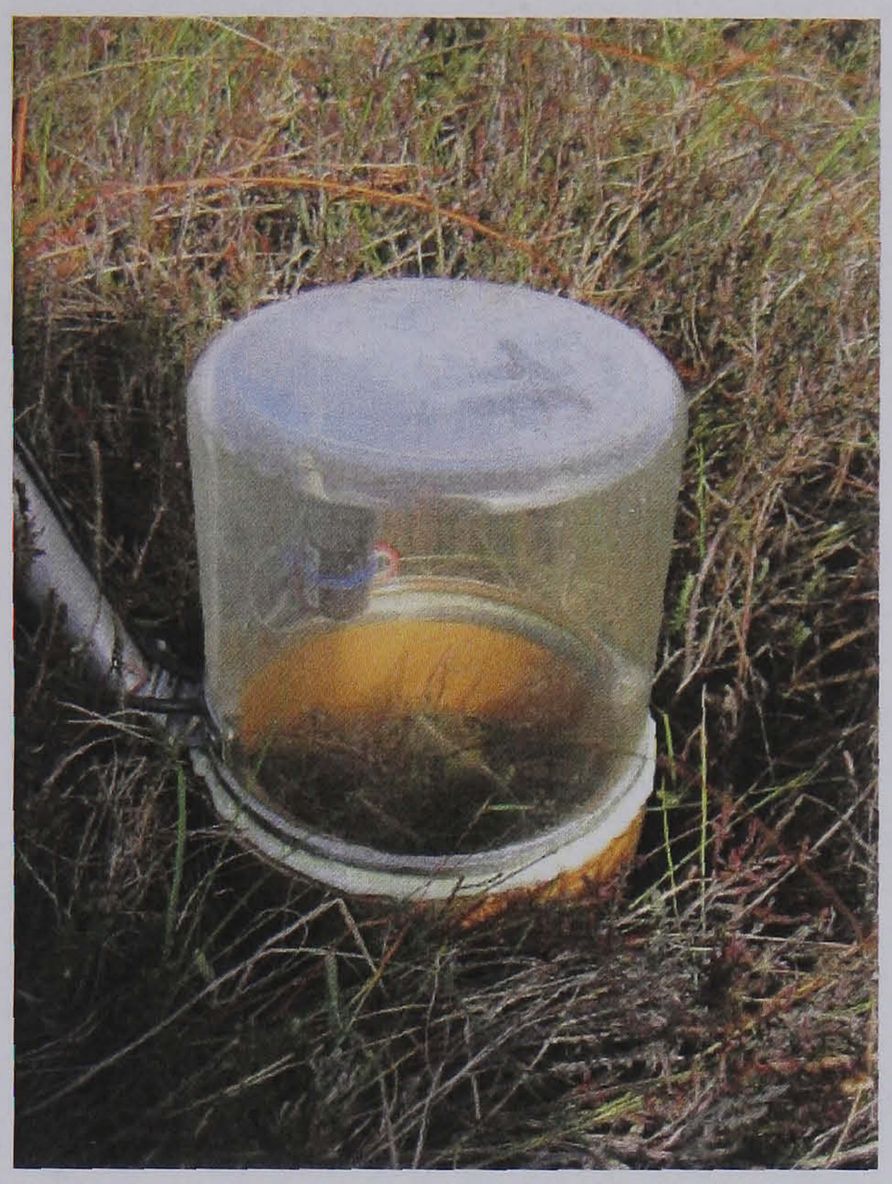

Figure 2.6 The IRGA's clear acrylic chamber in operation on one of the fixed collars used for CO_2 measurements.

The chamber has a small fan installed to ensure that the air was well mixed within the chamber, but without creating pressure differentials within the chamber or on the peat surface. This fan also allows the chamber to be purged of gas in-between flux measurements and re-equilibrate the chamber with the atmosphere. An internal pump within the IRGA pumped the air from the chamber, via the copper manifold, into the IRGA sample chamber, and back again. Other sensors within the chamber include an air temperature probe, an atmospheric pressure sensor, and a PAR gauge.

The clear acrylic chamber was fitted onto the permanently installed collars at the field

site, a good seal between the collar and the chamber was ensured by having a tight seal between a small metal flange at the base of the chamber which fitted into the collar and a second seal was created between chamber and the collar using rubber sealant. The IRGA circulates air through the perforated copper manifold, into the IRGA, via silicone sampling tubes; this sample is then passed into a sample cell. The sample cell comprises of; a bulb emitting specific quanta of an infra-red wavelength, a known length sample cell, and a phototransistor for measuring the amount of the infra-red light received. From the amount of the infra-red quanta received by the phototransistor, and the amount of quanta emitted by the infra-red bulb, the amount of CO_2 within the sample cell can be calculated. The air is then circulated back into the chamber to ensure that the peat is not forced to artificially flux CO_2 by either pressure or concentration gradients. Air from the chamber is circulated on a continuous basis for between 2 and 5 minutes depending on air temperature. The IRGA measures CO_2 in parts per million by volume (ppmv) concentration every 4-5 seconds, and from this a flux measurement was constructed, which is described latter in this section.

The second method for measuring CO_2 and CH_4 again uses a closed chamber method. A chamber with; a clear acrylic window in the top, two small holes, a suba-seal™, and opaque walls were fitted onto the permanently fitted collars (Figure 2.7).

Figure 2.7 Chamber with clear acrylic top and opaque sides in position on a permanent fixed collar adjacent to a piezometer.

The two small holes were sealed whilst the chamber was on the peat, and periodically attached to the IRGA via silicone tubes. The two silicone tubes were removed and the chamber resealed. Unsealing the chamber to attach the silicone tubes allowed the partial pressures within the chamber to equalise with the atmosphere as is one of the recommendations by Welles (2001). The IRGA displayed the CO_2 concentration in ppmv, which was then recorded. It was ensured that the silicone sample tubes were as close to the centre of the chamber as possible and the ppmv concentration was allowed to stabilise before being recorded. As several chambers could be fitted onto the peat surface, and the IRGA could sample one chamber after another rather than being attached to one chamber whilst a time series was taken, this meant that several chambers could be

left on the peat at the same time and for longer, which was beneficial when CO_2 fluxes were low, normally occurring in cold conditions. The chambers used in this sampling method were divided into light and dark measurements to ensure continuity with the other closed chamber sampling method.

Methane was sampled using the chambers with the clear acrylic top and opaque sides (Figure 2.7). Measurements of CH_4 were taken straight after CO_2 concentrations had been measured the by the IRGA, and involved using the suba-seal™, a syringe, and a glass vial fitted with a gas septum. The glass vials were pre labelled in the lab and once in the field, opened to equilibrate the interior of the vial with the atmosphere, and to release any gases that might interfere or contaminate the results during analysis. The vials were then evacuated using the gas syringe to remove twice the volume of the vial. The gases from the interior of the chamber were collected using the syringe and sampled through the suba-seal™. The syringe was pumped twice to ensure that the gasses within the chamber were mixed, and then the gas sample injected into the evacuated gas vial. The vial was then filled with more than twice the volume of the vial with the sample gas. These samples were analysed using a Gas Chromatograph (GC) at CEH Lancaster (Perkin Elmer Autosystem XL gas chromatograph using a Flame Ionisation Detector (FID). This GC sampled both CH_4 and CO_2 using a flame ionisation detector and a methaniser respectively. This method of measuring CO_2 with the IRGA and GC gave two measures of CO_2 taken at the same time using two different instruments. This enabled a comparison of methods of CO_2 collection using two different instruments and two different methods of gas sampling.

From these CO_2 and CH_4 concentration measurements a flux value was calculated. This calculation is based on the ideal gas law which states that:

$$PV = nRT \qquad \textbf{2.ii}$$

Where P = pressure, V = Volume of the system (l), n = number of moles, R = Universal gas constant (1 atm mol^{-1} K^{-1}), and T = Temperature (K). From this equation the weight of carbon dioxide in the chamber can be calculated using the following equation

$$G=1\times10^{6}[CO_2]V\left(\frac{p}{nRT}\right)M_r \qquad \textbf{2.iii}$$

Where G = weight of gas (g), $[CO_2]$ = Concentration of CO_2 (ppmv), V = Volume (l), p = Pressure (atm), n = number of moles, R = universal gas constant (1 atm mol^{-1} K^{-1}), T = temperature (K), M_r = relative atomic mass (g mol^{-1}).

Using this calculated weight the flux in the chamber can be calculated using the following equation

$$F=\left(\frac{C_1-C_0}{Time}\right)/SA \qquad \textbf{2.iv}$$

Where F = flux (CO_2 g^{-1} m-^{2} h^{-1}) C_1 = CO_2 weight within chamber at time 1 (g), C_o = CO_2 weight within chamber at time 0 (g), Time = time between time 1 and time 0 (h), SA = surface area (m^{-2}).

These equations were used to calculate flux values over several different time periods and concentrations to find an average flux value for each measurement.

2.3.6. Climatic measurements

The site was also monitored for; water table depth, PAR (Photosynthetically Active Radiation), rainfall, grip flow, conductivity, and soil air and water temperature. Water table depth was measured using a pressure transducers (PDCR1830 Campbell scientific) fitted in the piezometer position as shown in Figs 2.2, 2.4, and 2.6; these readings were made upon every site. PAR was measured using a Quantum sensor (SKP215 Skye Instruments). Rainfall was measured using a tipping bucket rain gauge (AGR100 Campbell Scientific Ltd.). Grip flow was measured using a pressure transducer and manual calibration for flow (PDCR1830 Campbell Scientific Ltd.). Temperature for soil, air and water were all measured using a temperature probe (107 temperature probe Campbell Scientific Ltd.). All data loggers (CRX10 Campbell scientific) collected data every four seconds and averaging to every fifteen minutes for each of these environmental variables.

2.3.7. Data analyses and statistics

In order to satisfy the objective; 'To determine the effect of water table restoration on CO_2 and CH_4 fluxes,' (see section 2.2) the transect data will be compared graphically, and then analysed statistically by multiple linear regression with the water table data collected from the piezometers and climatic variables (Soil temperature, air temperature, water temperature, PAR, and water table depth). Gross, net, and primary productivity

fluxes from these paired collars were measured over an eighteen month period and the results were analysed using a multiple linear regression approach to test the significance of water table depth to gaseous CO_2 flux in relation to other variables.

The second objective, posed in section 2.2; 'To examine the effects of seasonal climate variation on CO_2 and CH_4 fluxes,' will be achieved by analysing the results graphically and then statistically. Again, like the first question the statistical analysis will be a multiple linear regression, and will determine whether seasonality is an important controlling variable with regard to CO_2 fluxes over and above the influence of the variables used to answer the first question. The third objective (section 2.2) 'To determine whether season or treatment accounts for most of the variation in CO_2 flux' will be achieved by using partial correlation to determine the partial correlation coefficients, which will give a measure of the significance of each variable.

Multiple Linear regression studies the relationship between several independent or predictor variables and a dependent or criterion variable. In this case the criterion variable is a flux estimate which, in the case of this study will be: gross flux, net flux, and primary productivity flux. The variables measured are soil, air and water temperature, PAR (Photosynthetically active radiation), season (Defined as month number with January = 1, December = 12), depth to water table, and collar number. Of these variables, soil, air and water temperature, PAR, and water table depth were also logged so that power law relationships could also be considered in the analysis. For inclusion, all variables were considered at the 95% significance level.

Partial correlation studies the relationship between two independent variables where the variability of a common set of regressors have been accounted for. In this study, to answer the hypothesis that season will account for the greatest proportion of the changes in fluxes over the year, whilst treatment will account for the magnitude at which CO_2 is released, partial correlation was applied to gross, net, and primary productivity flux estimates. The variables used were gross, net, and primary productivity fluxes, soil temperature, PAR, water table depth, season, and collar number. To find the partial correlation coefficient between two variables, for example water table depth and gross CO_2 flux, the effects of the other variables were removed by multiple linear regression, and the residuals outputted. For example gross CO_2 flux was regressed against soil temperature, season, PAR, and collar and the residuals from this regression stored as an output. Water table depth also had the same variables regressed and the residuals outputted. The two sets of stored residuals from gross CO_2 flux and water table depth were then regressed to give the partial correlation coefficient. This partial correlation coefficient is then a direct measure of the importance of that variable, e.g. water table depth, to flux. This process was applied to all of the variables to find the most important correlation.

The final objective to be completed; 'To calculate the carbon budget for a restored peat,' can be achieved in several ways. In this project it was answered by both interpolation and extrapolation methods. The first method, applied to the meteorological data to define an export budget for the field site, was via an extrapolation method, and modelled the

carbon fluxes, with respect to the significant variables found from the multiple linear regression study. This was carried out to answer the hypothesis that 'Restoration of the water table depth in a drained upland peat will reduce the overall CO_2 fluxes and increase the CH_4 fluxes from the peat surface'. These significant variables will then be used to model the CO_2 fluxes and scaled up temporally and spatially to give an export value for the field site. Diurnal variation was account for in the modelled data by using data measured every 15 minutes by the data loggers. When PAR was zero the formula applied to the data ensured that the flux value was purely derived from the respiration part of the equation (Equation 2.viii). This modelling technique is calibrated using field measurements of net and gross CO_2 flux, and the equations are taken from the regression analysis and a literature review.

The second method applied to the data was an interpolation method and assumed the fluxes change on a linear scale between the flux readings and these estimates were then scaled up over the time course of the observations. Diurnal variation was assumed to be accounted for by measuring the CO_2 fluxes at representative times of the day, where the flux was not at a maximum, or a minimum, but an average of the two, and represented an average flux for the day. To test whether this is an accurate assumption the measured CO_2 fluxes over a larger spatial scale, can be correlated against the CO_2 fluxes from the transect to see whether they are statistically similar. A more in depth analysis of the equations and time periods used to predict the carbon budget from the field site, are discussed in chapter 6.

So from this seeming simple experimental setup, measuring CO_2 fluxes in relation to water table, a series of questions about the carbon budget of the Hexhamshire common field site can be answered.

2.4. Results

This section describes the results found at the Hexhamshire Common field site and the effects of water table restoration on CO_2 and CH_4 fluxes. This results section defines the effects of seasonal climate variations on the CO_2 and CH_4 fluxes, and the magnitude of effects of season treatments on CO_2 fluxes. The last section in the results defines literature models for predicting CO_2 and CH_4 fluxes from the field site and applies them to the Hexhamshire Common field site and compares these values to measured values of CO_2 and CH_4 fluxes.

2.4.1. Water table restoration effect on CO_2 fluxes

2.4.1.1. Gross CO_2 fluxes

Restoration of the water table on upland peat should reduce the overall CO_2 fluxes. The simplest way to test this hypothesised relationship is to average the gross CO_2 fluxes over a year and plot a simple chart with the corresponding averaged yearly water table depths (Figure 2.8).

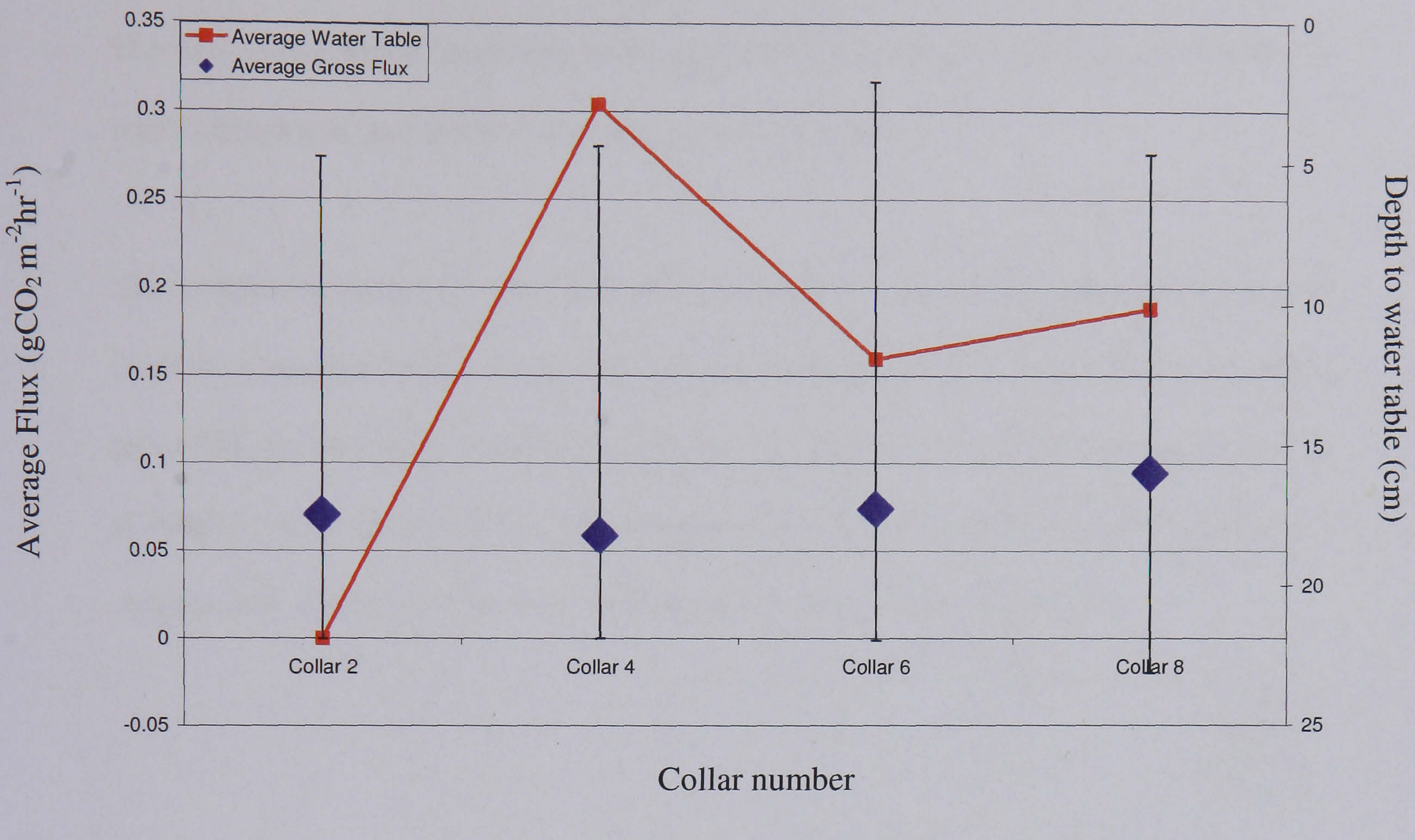

Figure 2.8 Yearly average gross CO_2 for each collar with an average water table depth overlay

Looking at the averaged data comparatively shows Figure 2.8 to have no visual relationship between the water table depth and gross flux. From the hypothesis it would be expected that the collar with the greatest annual average depth to water table would also have the greatest annual gross CO_2 flux. The collar with the greatest annual average depth to the water table is collar 2 and as can be seen from Figure 2.8, collar 2 has an intermediate release of gross CO_2 when compared to the rest of the gross flux collars. The collar with the greatest gross flux of CO_2 is collar 8 which has the second shallowest annual average depth to the water table. Collar 6 has a slightly deeper average water table when compared to collar 8 and so according the hypothesis should have a greater flux value, but can be clearly seen to have a lower gross flux value than collar 8. Collar 6

has a similar gross flux value to collar 2, but their water table depths are very different. The only collar which holds true to the hypothesis is collar 4, which has the shallowest water table depth, and the lowest average gross flux value.

The variation of gross CO_2 flux (Collars 2, 4, 6, and 8) over the year should also manifest itself as a seasonal effect, when temperatures are higher and the water tables are lower; gross CO_2 levels will be hypothesised to increase. Therefore a simple plot of gross CO_2 (Collars 2, 4, 6, and 8) release against their respective water table depths should yield a straight line. However, this is not the case as can be seen from Figure 2.9.

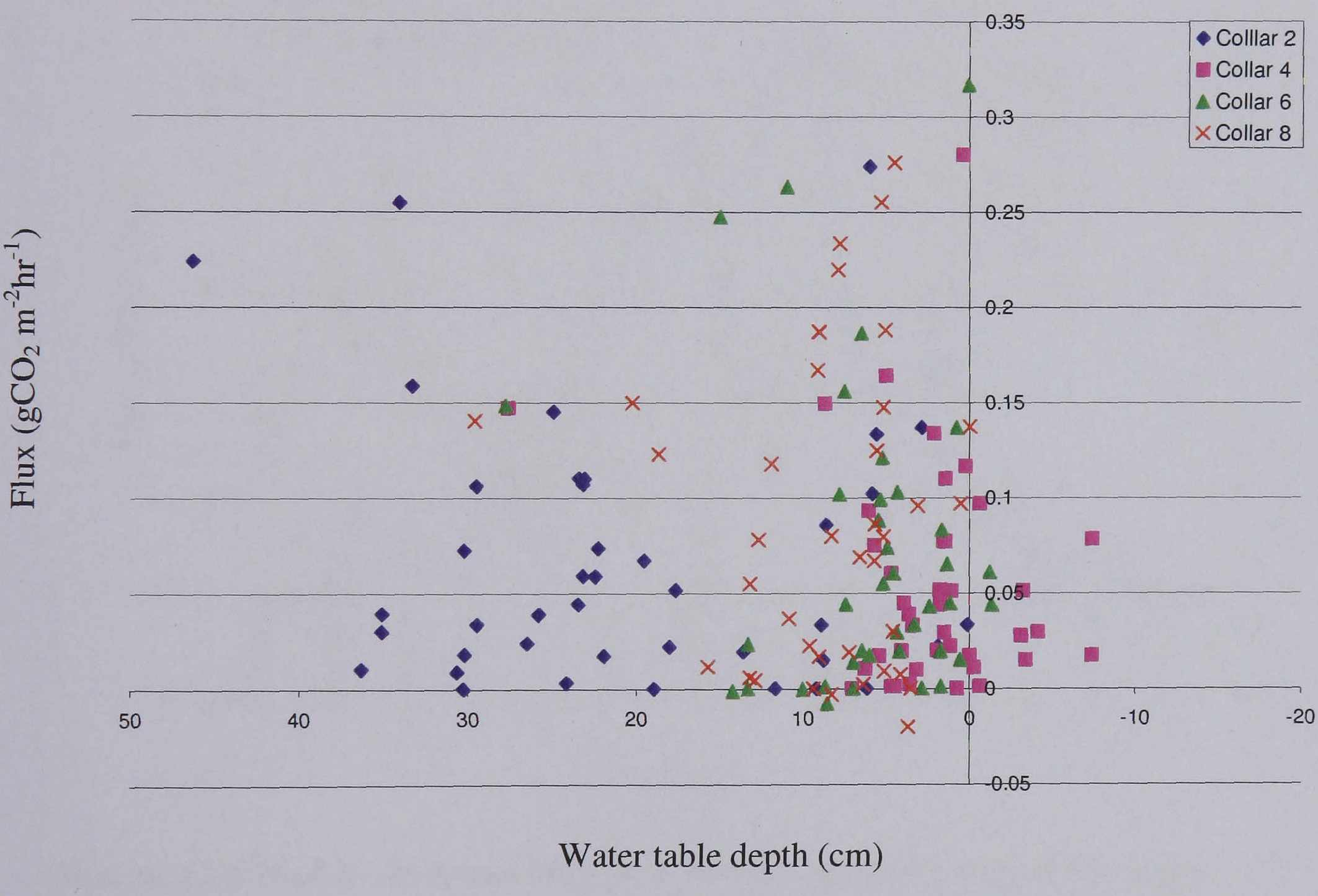

Figure 2.9 Gross CO_2 flux against water table depth for all measurements over the study period

The gross fluxes from Figure 2.9 can be seen to be almost uniform across all the

measurements, with most of the flux measurements falling between 0 and 0.1 $gCO_2\ m^{-2}h^{-1}$.

Having found no relationship so far between water table depth and gross CO_2 flux a visually comparative seasonal effects of gross CO_2 flux and water table depth were plotted for the average deepest water table and the average shallowest water table, should show some similarities with large rainfall events or drought periods (Figure 2.10).

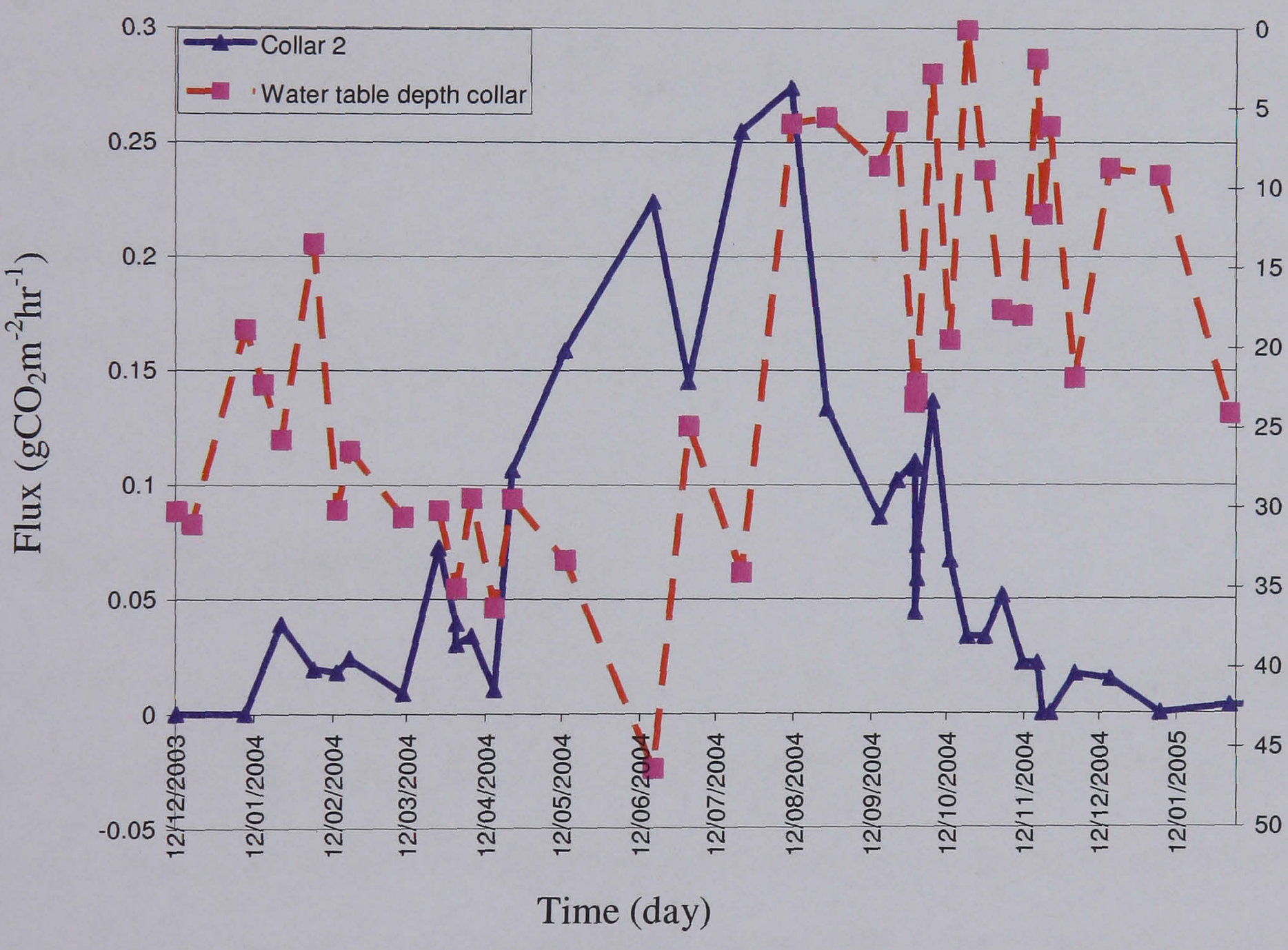

Figure 2.10 Maximum gross flux and corresponding water table depth

As can be seen from this simple visual comparison (Figure 2.10) it can generally be stated that the fluxes are lower when water tables are high, and fluxes are higher when

water table depths are lower. There is also an event in the middle of the sampling period on the 1/07/07, which shows that there is a large rainfall event, and a corresponding decrease in the gross flux measurements, however this relationship cannot be seen for other large water table depth changes. To prove whether this relationship is significant at statistical analysis will be performed on the data.

Applying multiple linear regression to gross CO_2 fluxes and using soil, air, and water temperature, PAR, season, water table depth, collar number, and the logged values of soil air and water temperature, PAR, and water table depth as variables, showed that there was a significant relationship at the 95% probability level between gross flux and soil temperature (P= 0.003, R^2 = 56.9%, n = 140, Gross flux = 0.0168 Soil Temperature-0.0248), and collar number (P = 0.049, R^2 = 0.2%, n =148). Therefore, a statistically significant effect between gross CO_2 flux and water table depth cannot be found.

2.4.1.2. Net CO_2 fluxes

The proposed hypothesis that; 'Restoration of the water table depth in a drained upland peat will reduce the overall CO_2 fluxes and increase the CH_4 fluxes from the peat surface,' would also suggest a weak relationship between the net fluxes and water table depth as net flux was measured independently of gross flux. This relationship should be harder to see as there may be an overlaid relationship of net fluxes with PAR values.

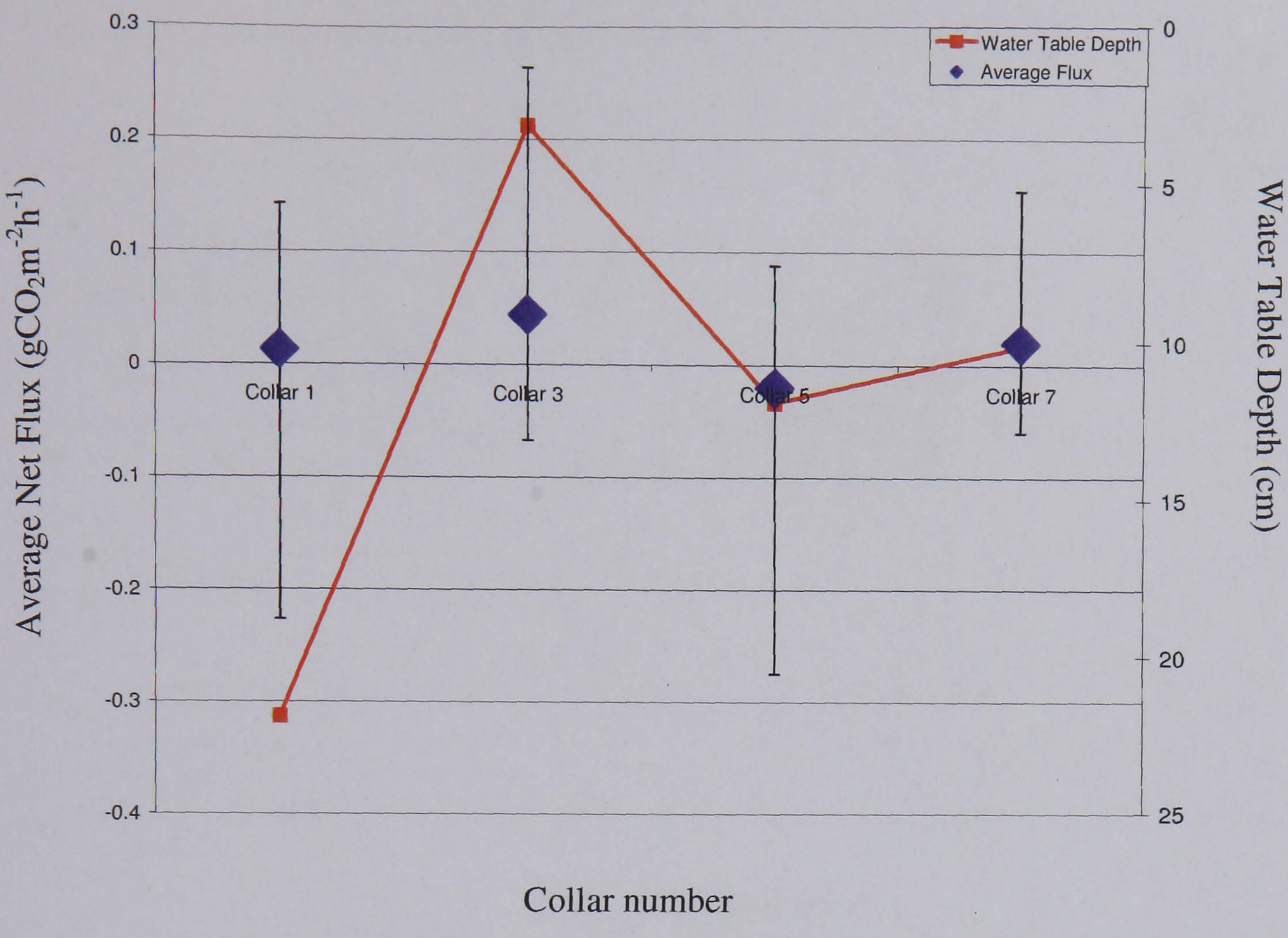

Figure 2.11 Yearly average net CO_2 flux for each collar with an average water table depth overlay

From the graph, no obvious relationship between the net fluxes and the water table can be observed (Figure 2.11). The net collar which should have the largest CO_2 release, according to the hypothesis should be collar 1, however collar 1 has the second lowest release of CO_2, whilst the collar which should be releasing the least amount of carbon because it has the highest water table is collar 3, but can be seen that collar 3 has, in fact, the highest release of CO_2.

As with the gross flux collars the net flux collars should have a seasonal relationship between water table and CO_2 flux. Therefore a plot of water table depth against corresponding net CO_2 flux should give a straight line graph.

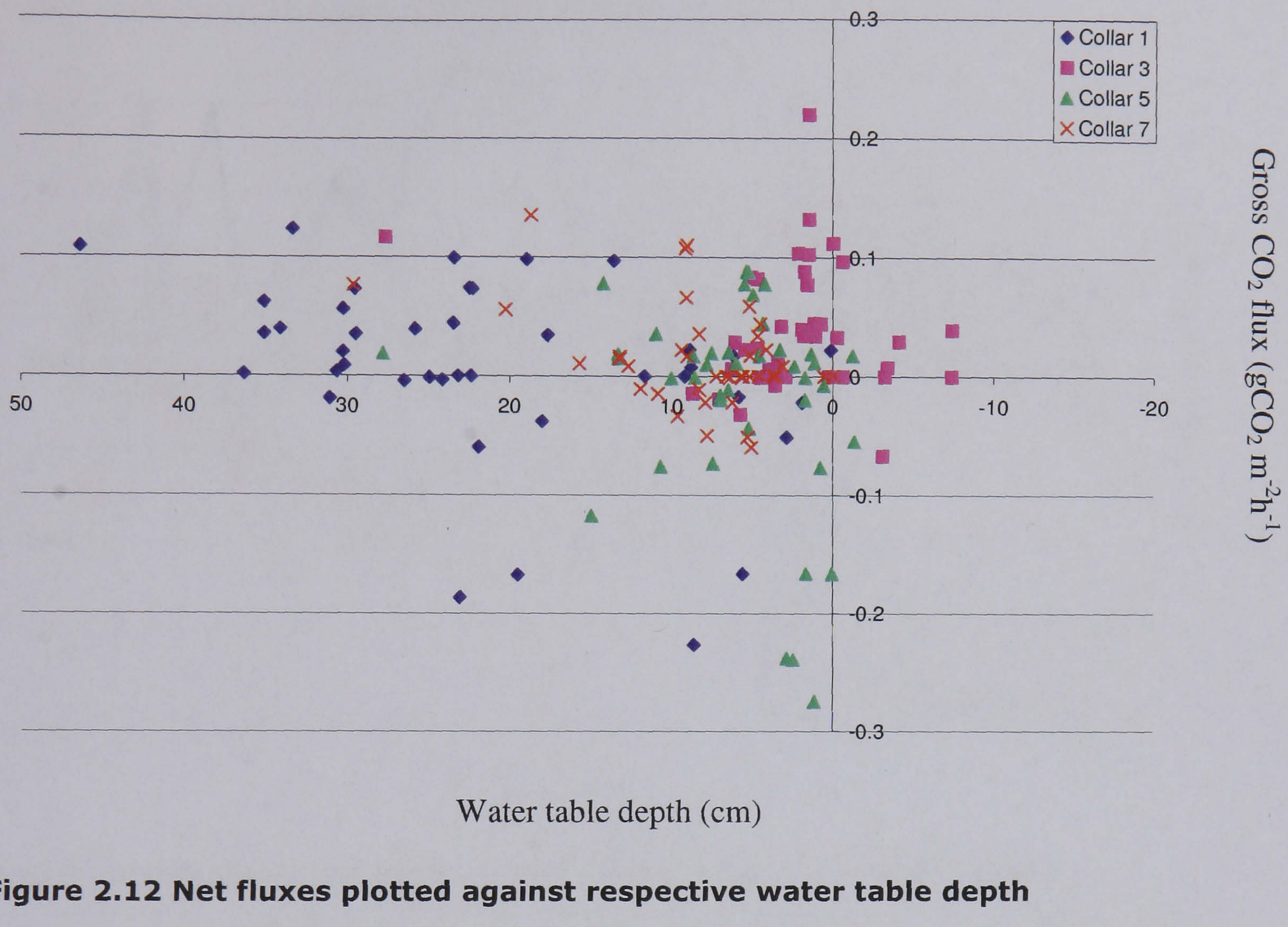

Figure 2.12 Net fluxes plotted against respective water table depth

As can be seen from Figure 2.12 there is no relationship between net fluxes and water table depth.

There may be a relationship between water table depth and seasonal fluxes, but is limited to large events such as a large storm or a rapid drying event. To see if there are any comparative changes in water table depth and net CO_2 flux a plot of the deepest water table depth and shallowest water table depth over time, as was done for gross fluxes (Figure 2.13).

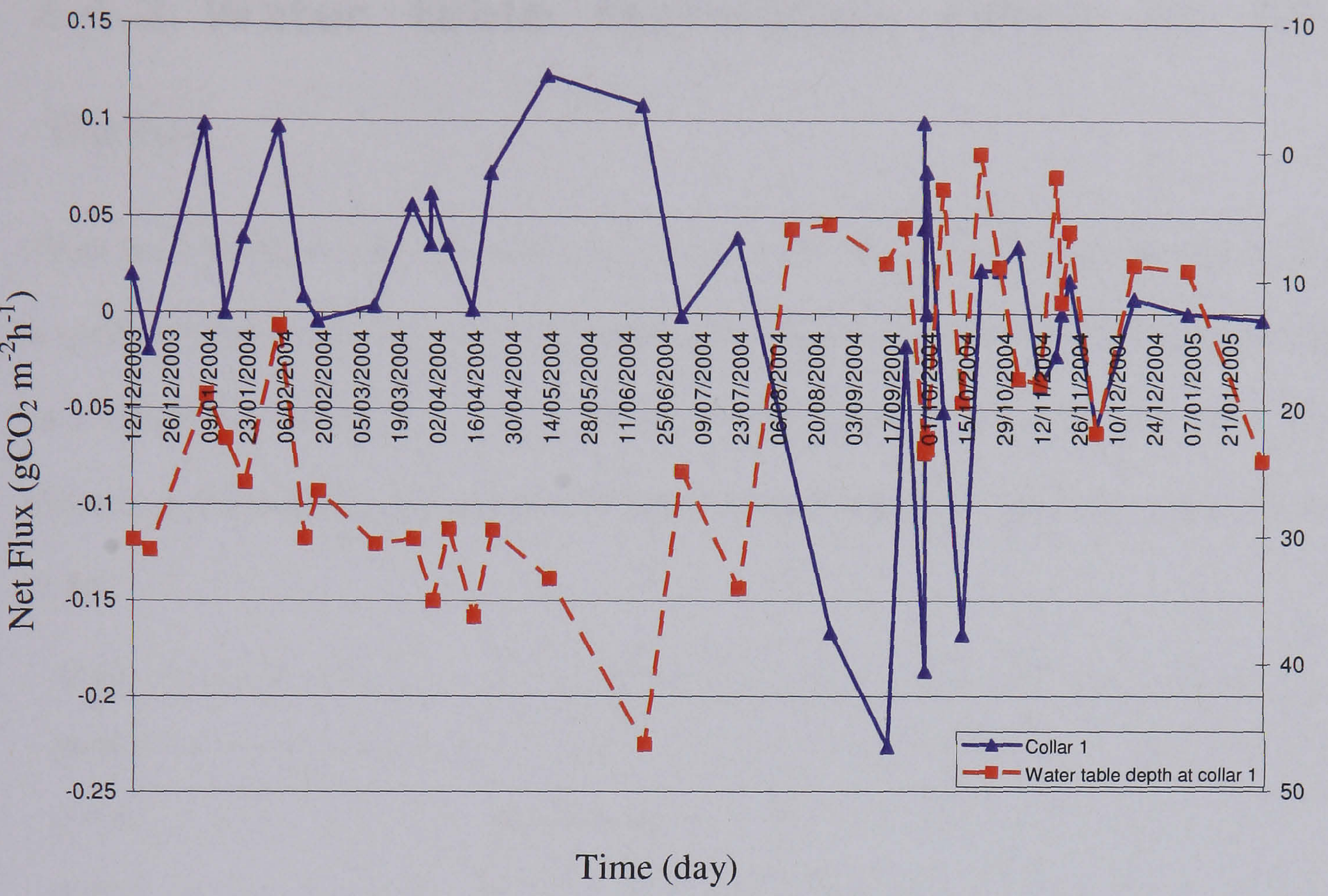

Figure 2.13 Maximum net flux with corresponding water table depth

Again, no visual relationship between large water table depth change events and changes in net CO_2 flux could be found.

To test where there was a statistical relationship between net flux and water table depth, the data was analysed by multiple linear regression using; soil temperature, photosynthetically active radiation (PAR), water table depth, and the logged values of soil, air, and water temperature, PAR, water table depth and season as variables. This analysis found a correlation between air temperature (P= 0.020), PAR (P = 0.001) and LOG PAR (P = 0.010) to be significant at the 95% confidence level. Therefore, there is no statistical relationship between water table depth and net CO_2 flux.

2.4.2. Water table restoration effect on CH_4 fluxes

From the hypothesis that CH_4 levels will decrease the lower the depth to the water table, a series of experiments were undertaken at the Hexhamshire Common field site. Looking at a simple bar chart of the average amount of CH_4 released during the year shows that there is a difference in the amount of CH_4 released depending upon the collar (Figure 2.14).

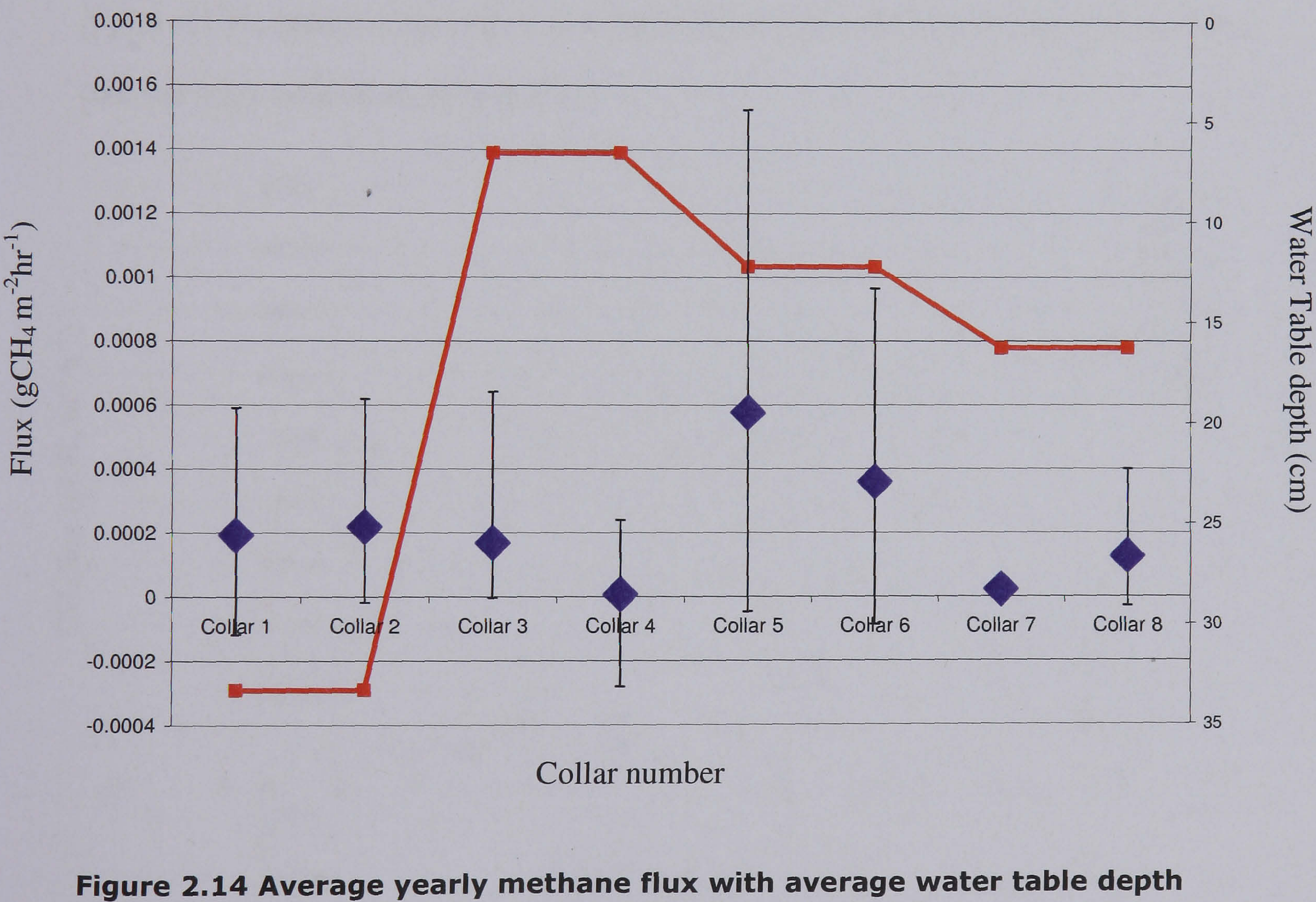

Figure 2.14 Average yearly methane flux with average water table depth

As the hypothesis states there should be a relationship to water table depth. Overlying average water table depth of the different collars shows that there is little relation to water table depth and CH_4 flux.

As can be seen from Figure 2.14, collars 3 and 4 have the highest water table depth but do not have the highest amount of flux, on average collars 3 and 4 do not have the lowest flux of CH_4 either. Collars 1 and 2 have the deepest water table depth and therefore should have the lowest amount of CH_4 release, but it clearly does not, neither does it have the highest amount of flux again if it is directly related to water table depth, it actually has the second highest flux of CH_4.

A plot of CH_4 against water table depth should show a seasonal relationship between CH_4 flux and water table depth (Figure 2.15)

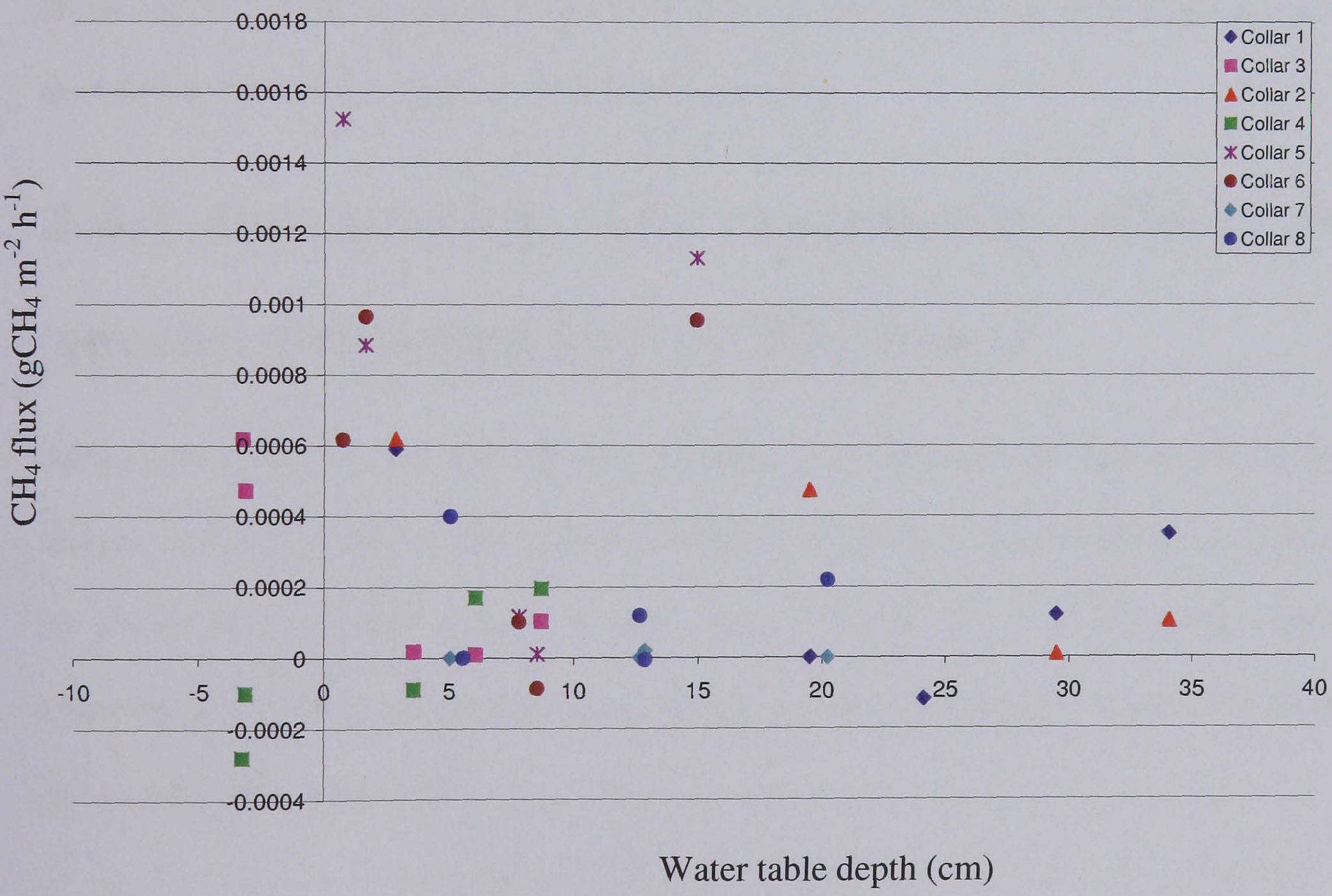

Figure 2.15 Methane flux against Water Table Depth

As can be seen from the graph (Figure 2.15) it can be said that CH_4 fluxes are generally higher when the water table is high, and are generally lower when the water table depth is lower. However, from the data there is a large spread of results and no one data set (Collars 1-8) can be shown to be representative of this inverse trend. The final test of the hypothesised relationship between water table depth and CH_4 flux is a statistical one. The data was analysing using multiple linear regression, where soil temperature, air temperature, water table depth, PAR, collar number, and logged values of; soil, water, and air temperature, and water table depth were used as terms in the regression anaylsis. Of these terms none of them were statistically significant over the 95% confidence level however the overall regression was significant ($P = 0.000$, $n = 30$) and explained 71.2% of the variance within the data. This means CH_4 also has no relation to the depth of water table below the surface, either positively or negatively.

2.4.3. Determining the magnitude effect of season and treatment on CO_2 fluxes

Partial correlation of CO_2 against the variables; soil temperature, water table depth, season, PAR and collar number showed, for gross fluxes that soil temperature accounted for the greatest amount of the variation within the data ($R^2 = 55.3\%$), and season accounted for a greater proportion of the data ($R^2 = 1.2\%$) compared to water table depth ($R^2 = 0.8\%$) (See Table 2.1)

	P	Correlation coefficient
Gross CO_2 residuals regressed against soil temperature residuals	0.000	55.3%
Gross CO_2 residuals regressed against water table depth residuals	0.292	0.8%
Gross CO_2 residuals regressed against season residuals	0.200	1.2%
Gross CO_2 residuals against PAR residuals	0.632	0.2%
Gross CO_2 residuals against collar residuals	0.044	3.0%

Table 2.1 Partial correlation coefficients for gross CO_2 flux

The partial correlation coefficients for net CO_2 fluxes show a different partial correlation coefficient significance, with water table depth accounting for a greater proportion of the variance (R^2 =5.5%) than season (R^2 =4.6%) (Table 2.2).

	P	Correlation coefficient
Net CO_2 residuals regressed against soil temperature residuals	0.446	0.4%
Net CO_2 residuals regressed against water table depth residuals	0.004	5.5%
Net CO_2 residuals regressed against season residuals	0.008	4.6%
Net CO_2 residuals against PAR residuals	0.762	0.1%
Net CO_2 residuals against collar residuals	0.881	0.0%

Table 2.2 Partial correlation coefficients for Net CO_2

The partial correlation coefficients for primary productivity shows that water table depth accounts for a greater proportion of the variance within the data (R^2 = 3.9%) compared to

season (R^2 = 2.3%) (Table 2.3).

	P	Correlation coefficient
Primary productivity CO_2 residuals regressed against soil temperature residuals	0.000	12.2%
Primary productivity CO_2 residuals regressed against water table depth residuals	0.014	3.9%
Primary productivity CO_2 residuals regressed against season residuals	0.060	2.3%
Primary productivity CO_2 residuals against PAR residuals	0.106	1.7%
Primary productivity CO_2 residuals against collar residuals	0.918	0.0%

Table 2.3 Partial correlation coefficients for primary productivity

So to summarise; water table accounts for the greater variation within the data for net CO_2 fluxes and primary productivity fluxes compared to season, whereas season accounts for the greatest variation within the data compared to water table depth for gross CO_2 fluxes.

2.4.4. Defining the effect of seasonal climate variations on CH_4 fluxes

Looking at the CH_4 fluxes over time is can be seen that the fluxes follow a similar pattern to gross CO_2 flux.

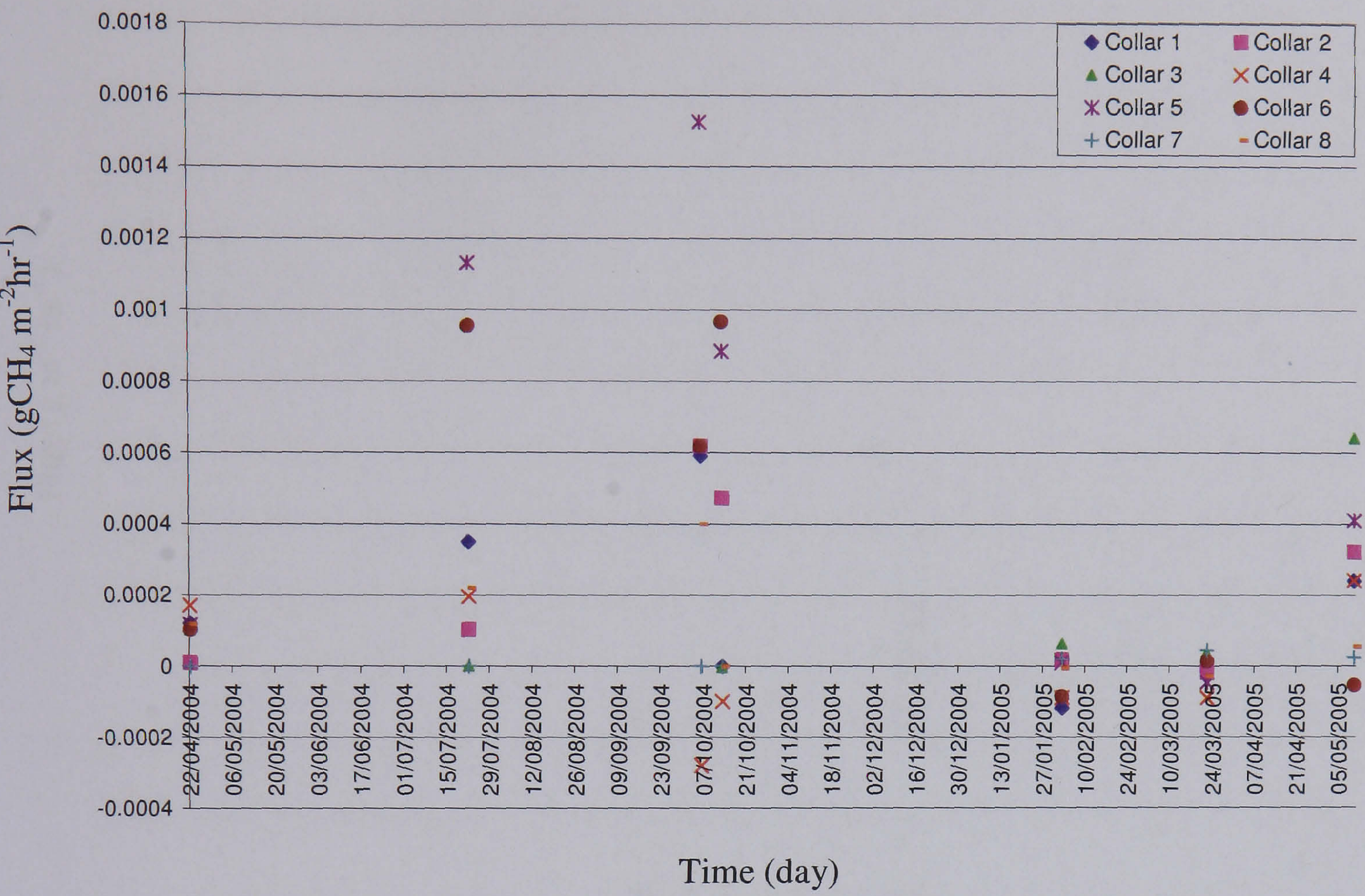

Figure 2.16 Methane fluxes over time

As can be seen from Figure 2.16 there is a low CH_4 flux at the start of the year which then increases as the seasons progress. There was an increase of CH_4 until a maximum of CH_4 is released on the 6/10/04. This is a similar date to the maximum amount of CO_2 released. Between the 22/7/04 and 6/10/04 of the CO_2 data encompasses the peak amount of CO_2 released. After the 6/10/04, the amount of CH_4 released decreases dramatically, and continues to decrease until the 22/03/05, when the fluxes start to increase again. As the fluxes have a similar pattern to the CO_2 fluxes it is thought that, like the CO_2 fluxes, the CH_4 fluxes will be dependant upon soil temperature to regulate CH_4 fluxes. A plot of soil temperature against CH_4 flux shows that there is no relationship between CH_4 and soil temperature (Figure 2.17).

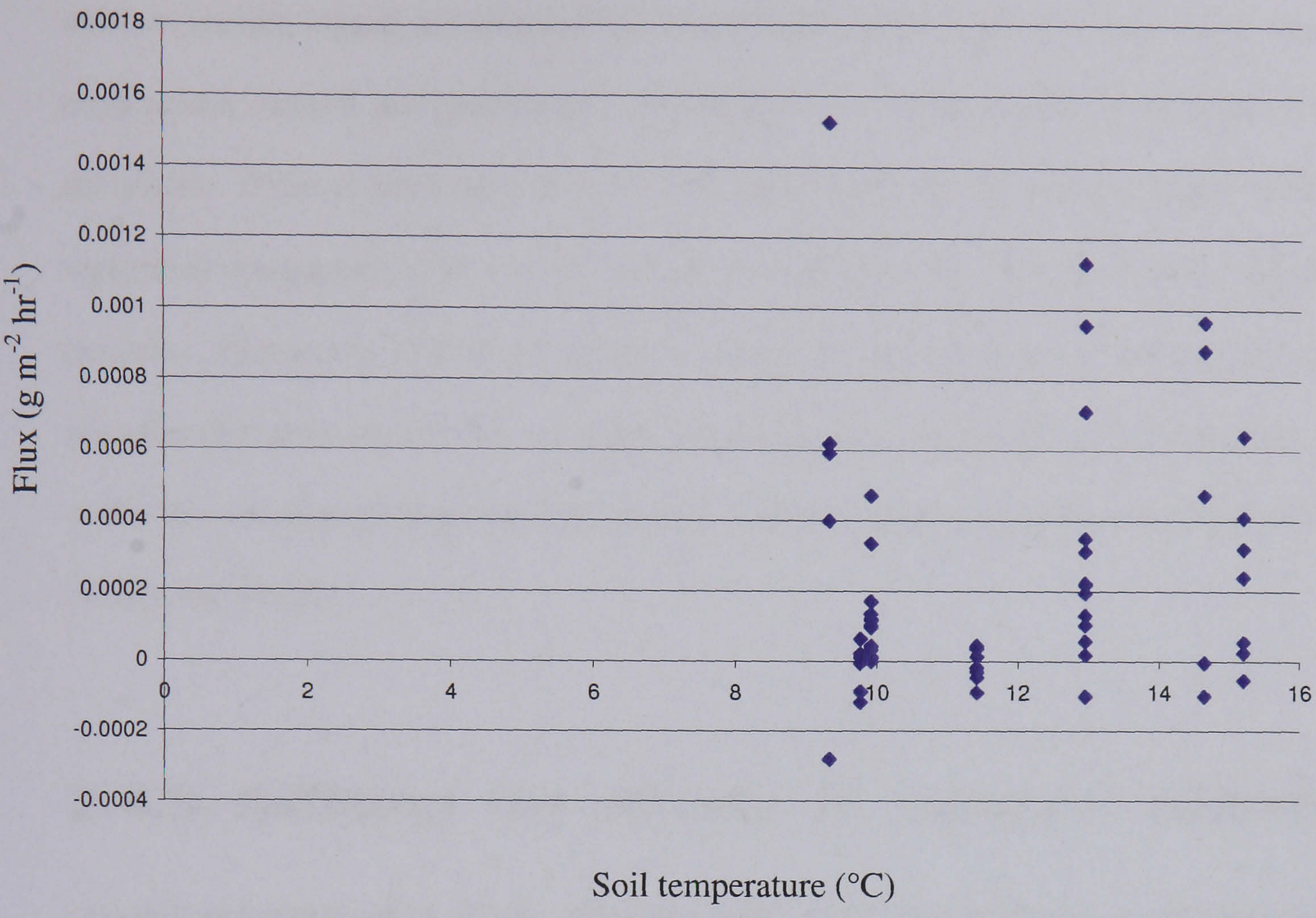

Figure 2.17 Methane Fluxes against soil temperature

As there are only a few results all the spatial and transect data have been included in the plot. The reason for little data is that several gas samples are collected at different time intervals from a chamber using a syringe and vial method, normally up to five, and then the CH_4 concentration within each vial is found using the GC. If a straight line cannot be plotted through the CH_4 concentration data over time then it is discarded. Also collecting and processing methane samples is time consuming, and therefore methane was sampled less often.

To try to find a statistical relationship between CH_4 and season, the data was analysed using multiple linear regression, where soil temperature, water table depth, PAR, collar

number, season, logged soil temperature, logged water table depth, air temperature, water temperature, logged air temperature, and logged water temperature were defined as covariates. Of these terms none of them were statistically significant however the overall regression was significant (P = 0.000, n = 30) and explained 71.2% of the variance within the data. This means CH_4 is not related to season or soil temperature, meaning that the microbes that produce the CH_4 are either not temperature controlled, or that the depth at which the microbes produce the CH_4 is well insulated against warming and cooling due to seasonal effects.

2.4.5. Defining the effects of seasonal climate variations on CO_2 flux and calculating a carbon budget

2.4.5.1. Gross CO_2 fluxes

Using the results from the multiple linear regression from section 2.4.1.1, showed that there was a significant relationship at the 95% probability between gross flux, soil temperature (P= 0.003, R^2 = 56.9%, n = 140) and collar number (P = 0.049, R^2 = 0.2%, n =148). Regressing gross CO_2 flux against soil temperature for each collar showed that linear correlation for individual collars with soil temperature varied from; R^2 = 71.0% (P = 0.000, n = 35) for collar 2 to 44.7% (P=0.000, n = 35) for collar 8. Soil temperature was measured at a 15 minute interval, and to try to predict the overall gross fluxes from the field site based on soil temperature a simple Arrhenius equation was applied to the

data. The aim was to model how the gross flux varied over the year to create an extrapolation method which accurately predicts gross CO_2 flux values from the field site and compare it to an interpolation method of flux values from the field site. Arrhenius equation is a simple linear equation which states that:-

$$Ln\ Flux\ \alpha n \frac{E_{act}}{T_{soil}} \qquad \textbf{2.v}$$

Where: Flux = the gross CO_2 flux ($gCO_2\ m^{-2}hr^{-1}$); E_{act} = the activation energy (Unitless); and T_{siol} = the absolute temperature of the soil (K). This is a basic form of the equation used by Lloyd and Taylor (1994). Predicting the flux from the field site using equations 2.vi to 2.viii, and regressing the predicted data with the actual data accounted for 41.7% of the variance (R^2 = 41.7% P = 0.000 n = 175). Using an annealing solving solution to find E_{act} gave the value of -763.01 (Unitless). A plot of flux against one over the soil temperature shows this correlation (Figure 2.18)

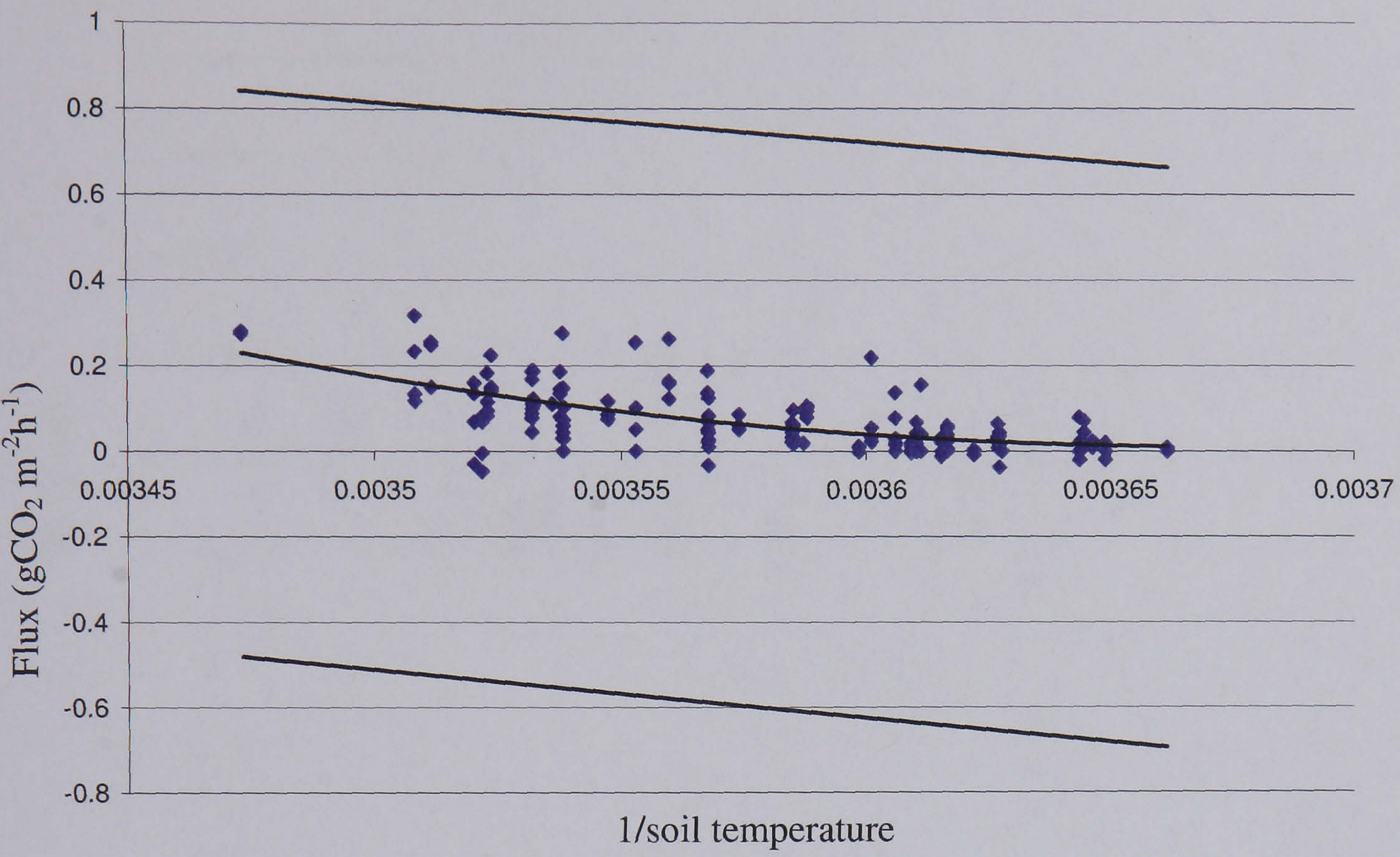

Figure 2.18 Gross CO_2 flux versus the reciprocal of the absolute soil temperature with maximum and minimum error lines.

As can be seen from the best-fit line, the relationship between soil temperature is not a linear one, and therefore an Arrhenius equation may not be the best equation to predict flux. A study of the residuals of this data shows that there is no systematic bias of either overestimation or under estimation of the gross fluxes (Figure 2.19), however the residuals have a wide spread at higher temperatures, suggesting the model is not a good fit at higher temperatures.

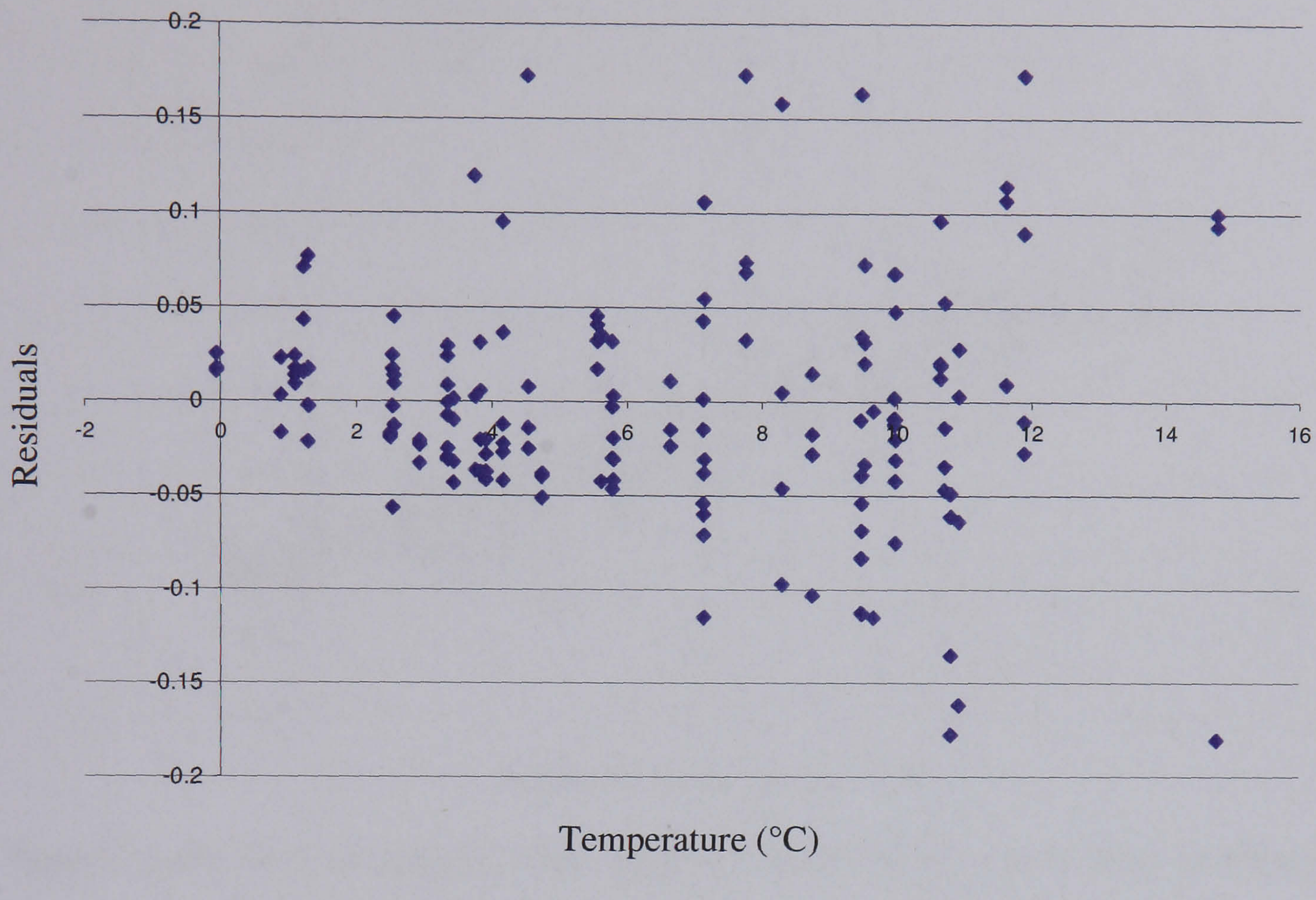

Figure 2.19 The residuals of predicted gross CO_2 flux regressed against actual gross CO_2 flux verses the reciprocal of the absolute temperature

A plot of the predicted values and the Arrhenius values shows a good visual correlation, but the R^2 = 41.7% suggests that the Arrhenius equations are good predictors of flux values, but not excellent (Figure 2.20).

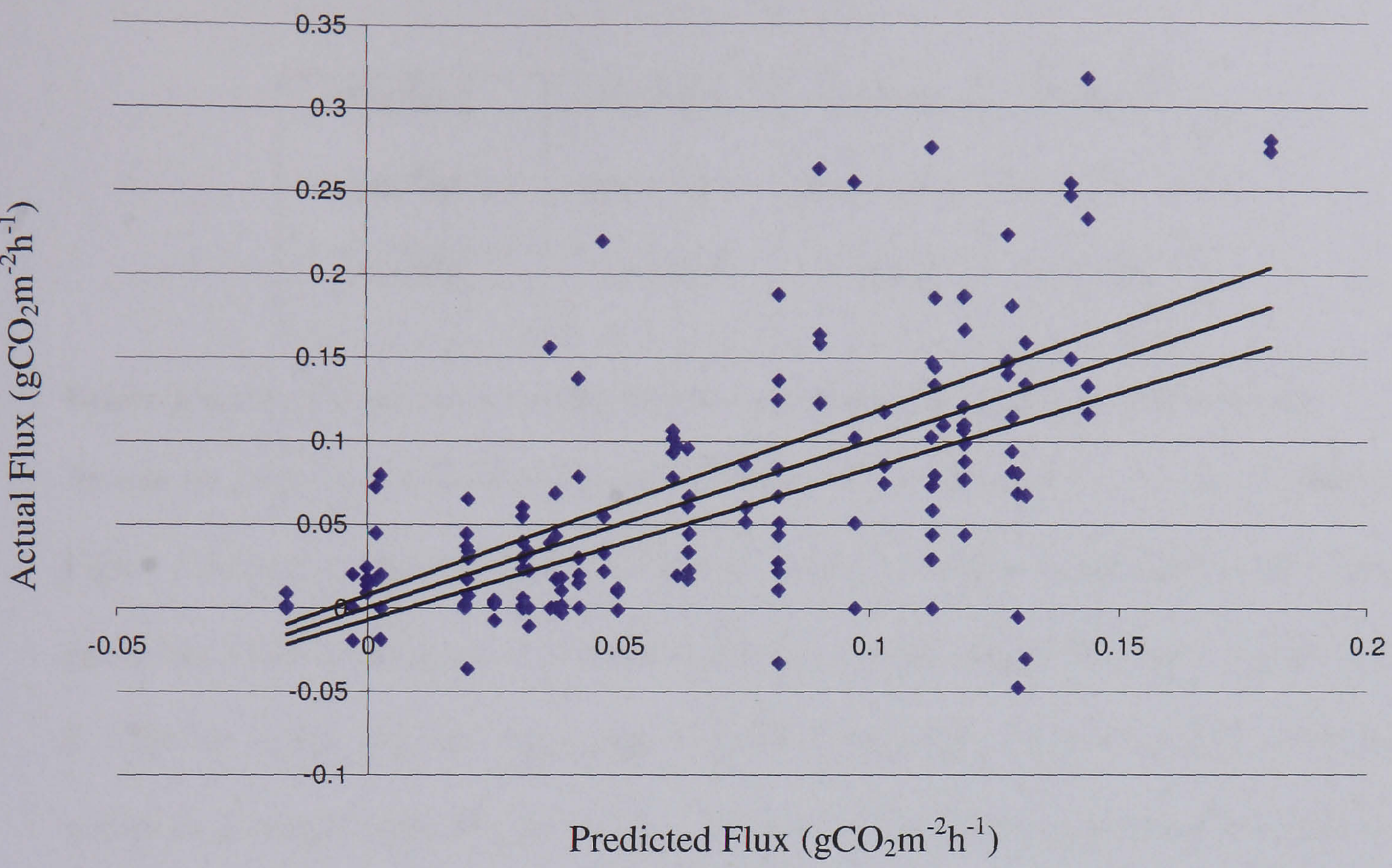

Figure 2.20 Plot of actual data and predicted data using the Arrhenius equation, with best fit minimum and maximum error lines.

Lloyd and Taylor (1994) prefer a more complex approach to predicting gross flux:

$$R = R_{10} e^{E_o\left(\left(\frac{1}{283.15-227.13}\right)-\left(\frac{1}{T_{soil}-227.13}\right)\right)} \qquad \textbf{2.vi}$$

Where: R = the gross flux value ($gCO_2\ m^{-2}hr^{-1}$); R_{10} = respiration rate of a collar at 10°C ($gCO_2\ m^{-2}h^{-1}$), E_o = activation energy (unitless), and T_o = a temperature between the soil temperature (T_{soil}) and 0K, T_{soil} = soil temperature (K). The Arrhenius equation and the relationship between gross flux and soil temperature was used to find the R_{10} value for all the collars and for the individual collars. If the reaction has a linear relationship between temperature and reaction rate, then this value will be constant across all collars. The R_{10} value when considering all of the collars is 0.1199 $gCO_2\ m^{-2}hr^{-1}$, the individual R_{10} values are given in Table 2.4

Collar 2 ($g\ m^{-2}\ hr^{-1}$)	Collar 4 ($g\ m^{-2}\ hr^{-1}$)	Collar 6 ($g\ m^{-2}\ hr^{-1}$)	Collar 8 ($g\ m^{-2}\ hr^{-1}$)
0.1284	0.0963	1.2205	0.1486

Table 2.4 R_{10} values of all collars where gross CO_2 flux was measured.

As can be seen from this table (Table 2.4) there are a range of R_{10} values. Looking at Figure 2.8 the R_{10} values would be expected to have a similar magnitude to the average gross flux of CO_2 for the year, however it can be seen the largest R_{10} value is from collar 6, which is nearly 10 times larger than the next smallest R_{10} value (Collar 8). This may not be an accurate approach for find R_{10} values as the relationship between the Arrhenius equation and gross flux is not a good predictor of gross flux. Indeed, when the gross fluxes were predicted with the Lloyd and Taylor equation (Equation 2.vi), and the respiration rate at 10^0C (R_{10}) predicted from the Arrhenius equation, and the Lloyd and Taylor equation (equation 2.vi) regressed against the actual measured gross flux data, it had a lower R^2 value than the Arrhenius regression (R^2 = 2.26% compared to R^2 = 41.7%).

A better approach would be to calculate the R_{10} value for each collar by using an annealing solution for the Lloyd and Taylor equation (Equation 2.vi) to give the individual best-fit R_{10} values by minimising the residuals between the actual gross CO_2 flux values and the predicted gross flux values for each flux reading. This approach gave an overall R_{10} value of 0.09836 $gCO_2\ m^{-2}\ hr^{-1}$ (Compared to 0.1199 $gCO_2\ m^{-2}\ hr^{-1}$ for linear regression value of R_{10} from the Arrhenius equation) –Table 2.5.

	Collar 2 ($g\ m^{-2}\ hr^{-1}$)	Collar 4 ($g\ m^{-2}\ hr^{-1}$)	Collar 6 ($g\ m^{-2}\ hr^{-1}$)	Collar 8 ($g\ m^{-2}\ hr^{-1}$)
Linear Regression R_{10}	0.1284	0.0963	1.2205	0.1486
Iteratively solved R_{10}	0.1097	0.0832	0.0866	0.1144

Table 2.5 R_{10} values for linear regression and iteratively solved solutions

From Table 2.5, the largest change in R_{10} values is collar 6 which reduced from an R_{10} value of 1.2205 to 0.0866056, and the overall R^2 of the predicted gross data regressed against the actual gross data increased from R = 41.7% (Arrhenius, best fit so far) to R^2 = 45.44% (Iteratively solved solution).

A different approach to calculating the R_{10} values for each collar type was to use the Lloyd and Taylor approach again (Equation 2.vi), but this time to calculate the gross flux for every reading for every collar based on soil temperature, and then calculate the R_{10} value based on the residual between the actual gross flux and the predicted gross flux using an iterative solving solution. This would then give a range of results from which the average R_{10} value can be found. The overall R_{10} value for the collars increased from 0.09836 $gCO_2\ m^{-2}\ hr^{-1}$ (Iteratively solved R_{10} solution) to 0.106596 $gCO_2\ m^{-2}\ hr^{-1}$ (Individual R_{10} iterative solutions and averaged) – Table 2.6.

	Collar 2 ($g\ m^{-2}\ hr^{-1}$)	Collar 4 ($g\ m^{-2}\ hr^{-1}$)	Collar 6 ($g\ m^{-2}\ hr^{-1}$)	Collar 8 ($g\ m^{-2}\ hr^{-1}$)
Linear Regression R_{10}	0.1284	0.0963	1.2205	0.1486
Iteratively solved R_{10}	0.1096	0.0832	0.087	0.1144
Individual iterative solutions and averaged R_{10}	0.0870	0.0757	0.1271	0.1365

Table 2.6 R_{10} values for linear regression, iteratively solved, and individual iterative solutions and averaged values

From Table 2.6 the R_{10} values have not changed too much from the iteratively solved R_{10} values, with the greatest change in R_{10} value being for collar 6 again. This method for predicting R_{10} values increased the overall R^2 values of predicted gross flux data against actual gross flux data from $R^2 = 45.44\%$ (Iteratively solved R_{10} values) to $R^2 = 47.63\%$ (Individual iterative solutions and averaged values).

Further to these results, a plot of the residuals from predicted gross fluxes from individual iterative solutions and actual gross results showed that there was a relationship between the residuals and soil temperature suggesting that the Lloyd and Taylor equation does not take into account all of the variation of CO_2 fluxes due to soil temperature (Figure 2.21).

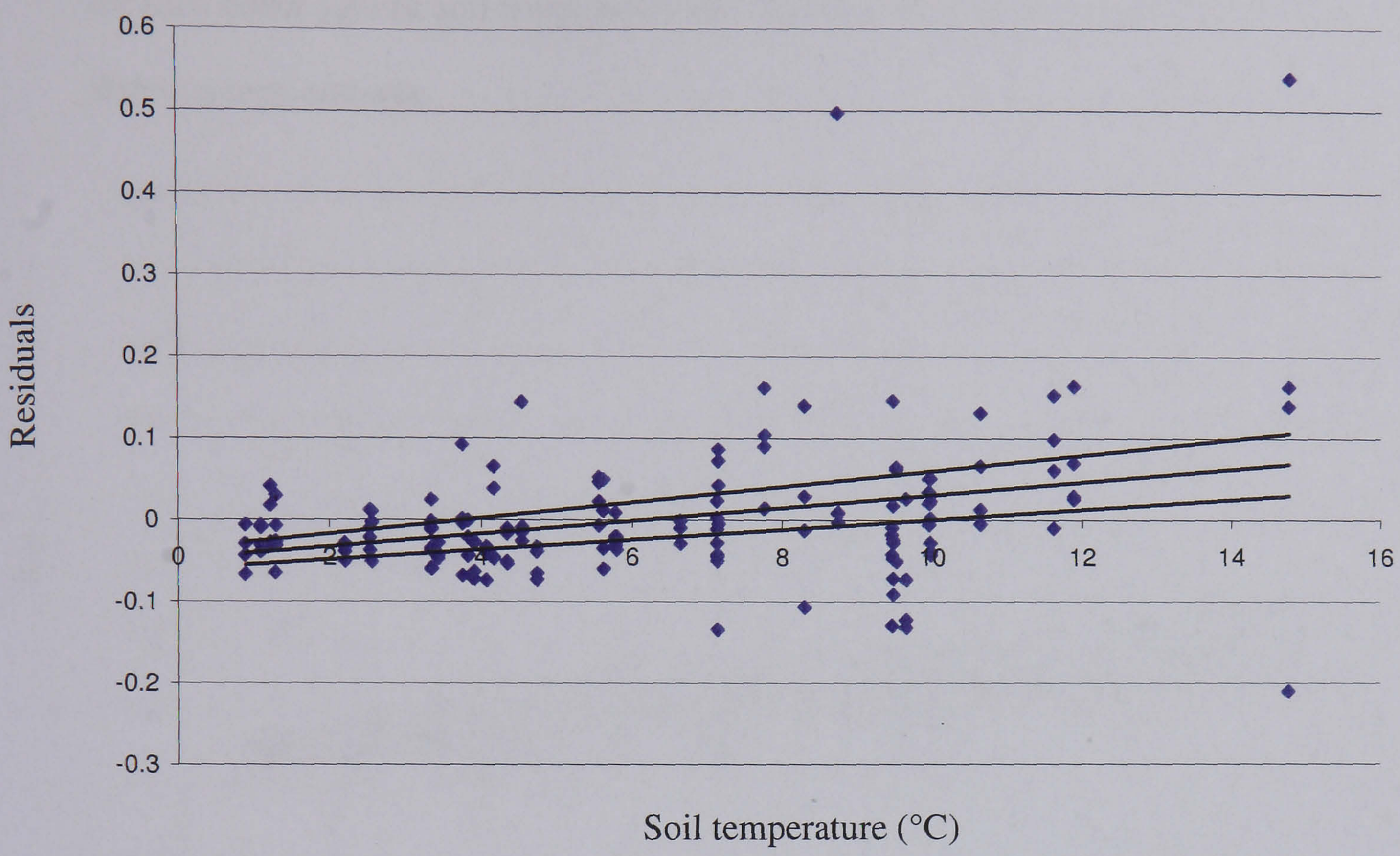

Figure 2.21 Residuals of predicted data, using Lloyd and Taylor equation, against actual data, plotted against soil temperature, with best fit, minimum and maximum error lines

This relationship is significant (R^2 = 11.1%, P = 0.000, n = 168) and would suggest that R_{10} is not a constant as defined by the Lloyd and Taylor equation (Equation 2.vi) and will vary with the soil temperature. As R_{10} is based on a biological term called Q_{10}, and is defined as:

$$LOG\ Q_{10} = \left(\frac{10}{T_2 - T_1}\right) \times LOG\left(\frac{K_2}{K_1}\right) \qquad \textbf{2.vii}$$

Where: T_2 = higher temperature (K), of the reaction, T_1 = lower temperature, K_2 = rate of reaction at the higher, K_1 = flux value at the lower temperature. If R_{10} is defined by temperature then regressing the accurately defined R_{10} values for each gross flux reading

for each collar against soil temperature should give a line which defines the R_{10} values at different temperatures.

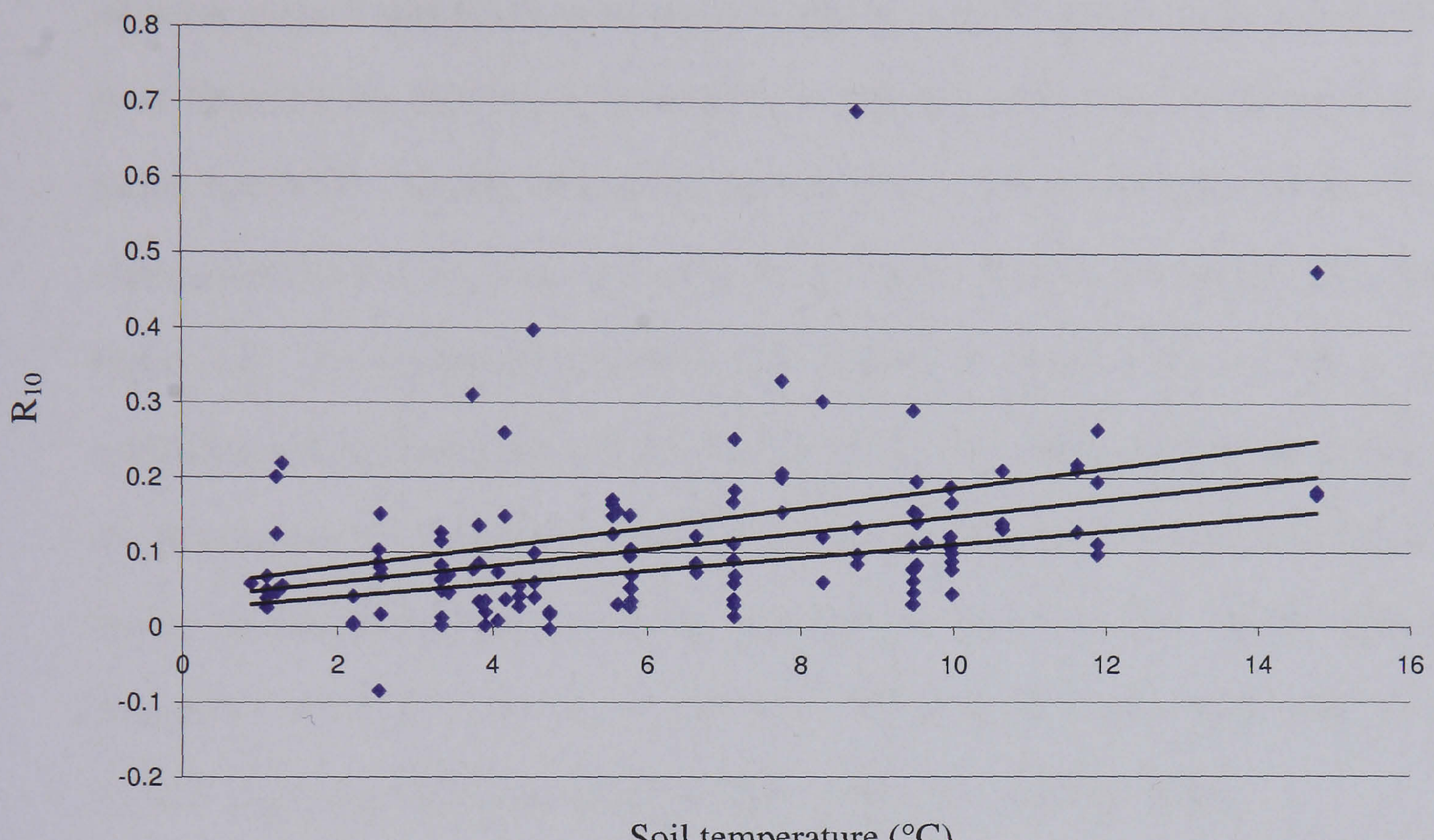

Figure 2.22 Graph of R_{10} values against soil temperature with best fit, minimum and maximum error lines

As can be seen from Figure 2.22, there is a relationship between R_{10} values and soil temperature (R_{10}=0.0111*soil temp+0.0374, R^2 = 15.3, P = 0.000, n = 148). Defining an equation for this line and substituting it into the Lloyd and Taylor equation (Equation 2.vi), and predicting gross CO_2 flux and regressing these values against actual gross flux data gave an R^2 = 43.95% for all the collars. When compared to the R^2 values for other common R_{10} values for the whole field site of 41.7% (Arrhenius), and 43.53% (Iterative solutions of individual readings and collars) show this to be the best way of predicting an overall R_{10} value for the field site. However, when the same is done for each individual collar and regression performed between predicted gross flux values and actual gross flux

values, then the R^2 value decreases to 4%, as this is such a dramatic decrease in R^2 value the equations were re-examined. The second order polynomial equation to define the R_{10} value for collar 8 was found to be negative, that is that the equation predicted that the gross fluxes for the year would be negative so that the collar would be taking up CO_2 during zero PAR. Clearly, this cannot be correct, as a simple average graph of collar eights gross flux over the year show collar 8 to be clearly positive, and releases CO_2, (See Figure 2.8). For simplicity the polynomial equation for collar 8 was left out of the regression, and predicted gross flux values for collars 2,4, and 6 were regressed against the actual gross flux values for collars 2,4 and 6. This gave an $R^2 = 43.45\%$, which is a poorer fit than both iterative solving solutions for the Lloyd and Taylor equation (Equation 2.vi) $R^2 = 45.44\%$ Lloyd and Taylor Iterative solution for each collar, $R^2 = 47.63\%$ Lloyd and Taylor individual iterative solution for each flux reading.

Overall the best method for predicting gross flux data is to iteratively solve the Lloyd and Taylor equation (Equation 2.vi), predicting R_{10} values for each reading and averaging the values for each collar. A scatter graph shows this relationship well.

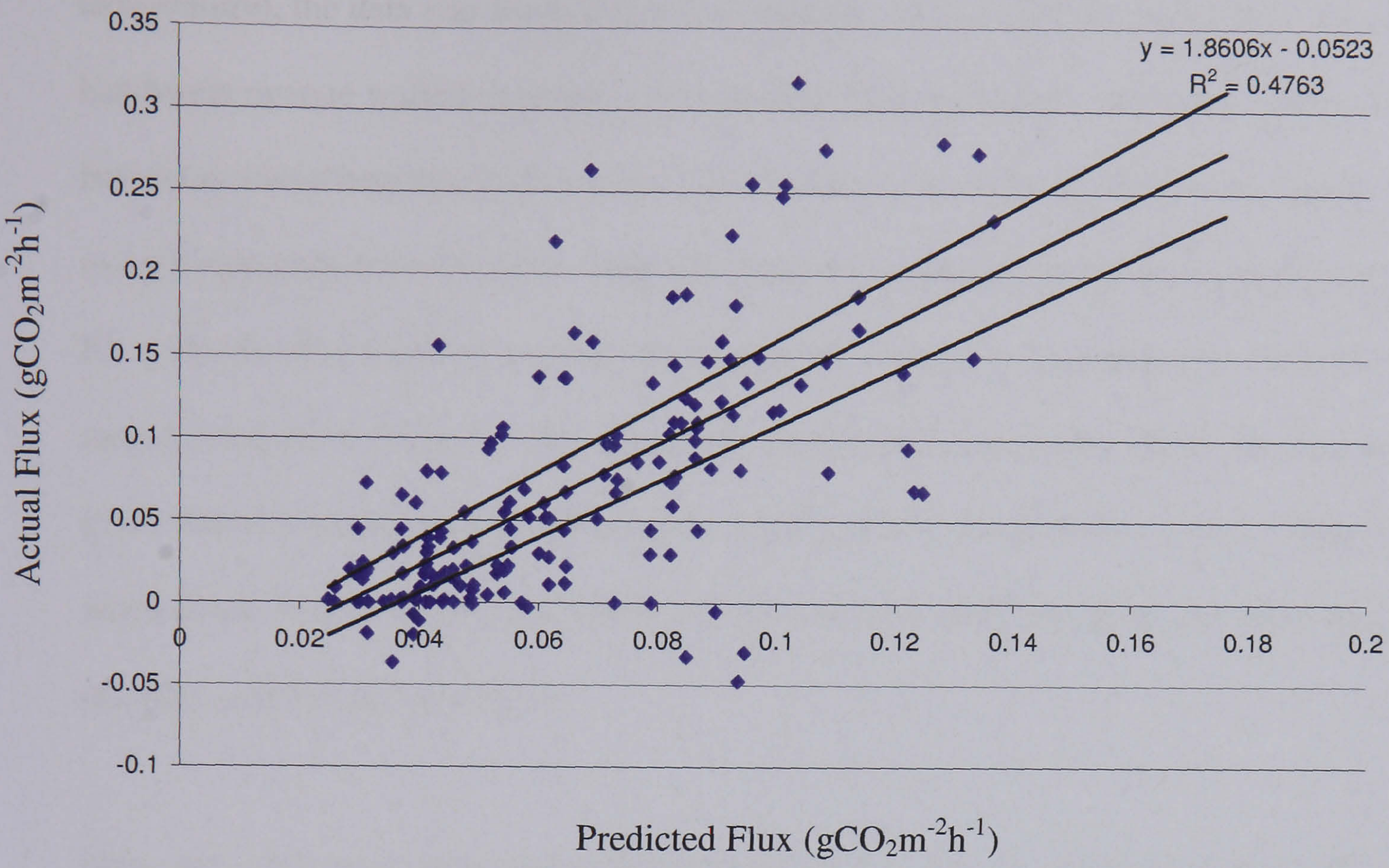

Figure 2.23 Measured CO_2 flux against Predicted CO_2 flux using Lloyd and Taylor (1994) equation with best fit and minimum and maximum error lines

2.4.5.2. Net CO_2 fluxes

When collecting net CO_2 data, two different types of chamber were used, the purpose built clear acrylic chamber and a series of handmade opaque walled chambers with clear top, for details of each chamber see section 2.3. When modelling the data over time according to the above equations (Equation 2.viii, and equation 2vi), if all the data was included from both chamber types (Clear acrylic purpose bought chamber, and handmade chamber with opaque sides and acrylic tops) then the correlation with the data with PAR was poor (R^2 = 6.9% P = 0.001 n = 165). Therefore to find any sort of relationship between the measured net flux values and their driving variables (PAR and soil

temperature), the data was looked at as two separate data sets (Clear acrylic chamber and handmade opaque walled chamber), in relation to PAR to find the best relationship. The best relationship between PAR and net CO_2 fluxes was with the net CO_2 fluxes measured using the purpose built chamber. Multiple linear regression of the net flux results gave an $R^2 = 20.4\%$ ($P = 0.000$ $n = 101$). Individual R^2 values for regression for each collar ranged from $R^2 = 70.13\%$ to $R^2 = 14.16\%$. Multiple linear regression of net flux with PAR from the opaque wall chambers gave an $R^2 = 8.1\%$ ($P = 0.024\%$ $n = 61$). Therefore when using data to predict net fluxes of CO_2 the data used was from the clear acrylic chamber supplied by pp systems.

However, when performing statistical analysis of the data all the results for net fluxes were used. The data was analysed by multiple linear regression using; soil temperature, photosynthetically active radiation (PAR), water table depth, and the logged values of soil, air, and water temperature; PAR, water table depth and season as variables. This analysis found a correlation between air temperature ($P= 0.020$), PAR ($P = 0.001$) and Log PAR ($P = 0.010$), air temperature significance is an expression of how gross fluxes change with soil temperature, which is controlled by air temperature. The fact that both PAR and logged PAR are significant suggests that the relationship between net CO_2 fluxes and PAR is non-linear, therefore to model the relationship of net CO_2 flux over the year a non-linear equation must be used if PAR is a driver of net CO_2 fluxes. A literature review revealed that there are two different types of equations that are used to predict net CO_2 in relation to PAR. The first is from Bubier *et al* (1998) and shows the relationship between NEE (Net Ecosystem Exchange) and PAR (Photosynthetically Active Radiation)

to be:-

$$Net\ Flux = \left(\frac{GP_{max} \times \alpha \times PAR}{\alpha \times PAR + GP_{max}} \right) + Gross\ Flux \qquad \textbf{2.viii}$$

Where α (Alpha) = initial slope of a rectangular hyperbola (also called the apparent quantum yield), GP_{max} +/- R = NEE asymptote and R = y axis intercept (or dark respiration value R<0).

Taking GP_{max} and α to be constant and measuring PAR, Net Flux and Gross Flux, and taking the sign convention to be the standard micrometeorology notation, where uptake of CO_2 is negative and CO_2 release is positive. Then substituting data into the equation for PAR, Net flux, and Gross Flux the constants were predicted by plotting a hyperbola of primary productivity fluxes against PAR, GP_{max} is defined by the maximum amount of CO_2 taken up, and α is defined by the linear part of the hyperbola equation.

Collar Number	α	GP_{max}
1	-0.0008133417	-0.31243068
3	-0.000332415938	-0.331819
5	-0.000838549	-0.483455645
7	-0.000369521953	-0.306133

Table 2.7 α and GP_{max} values used in the Bubier *et al.*, (1998) equation

In literature, GP_{max} is a commonly used term and is not necessarily related to the maximum PAR a site receives as gross productivity (GP) will plateau as PAR ceases to become a rate limiting step. Several factors will affect GP_{max}, namely all the factors

which affect plant growth (PAR, soil moisture, nutrients, and temperature). In the literature GP_{max} is defined as an extremely localised site specific constant (Bubier *et al.*, (1998) as GP_{max} will vary with the amount of vegetation within each collar. Therefore, a more representative measure would be to relate GP_{max} to; PAR level; the volume of plant material within the chamber; and type of plants within the chamber, as different plants take up different amounts of CO_2. For an estimate of gross flux the Lloyd and Taylor (1994) equation was substituted into the Bubier equation.

Regressing measured net fluxes against predicted net fluxes using Bubier's equation with Lloyd and Taylor's equation used to predict gross flux (Equation 2.viii), accounted for R^2 = 28.87% of the variance. As this does not account for a very large proportion of the variance of the net data another equation from literature was studied. This equation comes from Nykänen *et al.* (2003). Which has the form of:

$$Net\ Photosynthesis = \left(\frac{GP_{max} \times PAR}{PAR + K}\right) + b_0 + t \times T_{air} \qquad \textbf{2.ix}$$

Where Q = asymptotic maximum value of photosynthesis in optimal light conditions ($gCO_2\ m^{-2}h^{-1}$), PAR = solar irradiation, ($\mu mols\ m^{-2}s^{-1}$), k = half saturation parameter ($\mu mols\ m^{-1}s^{-1}$) i.e. the amount of radiation when photosynthesis is half of the maximum. B_o and t = constants, and finally T_{air} = air temperature (K).

This equation differs in the fact that there is; a temperature component to the equation; α has been eliminated; GP_{max} has been eliminated from the bottom row of the first part of the equation; a new term, K ahs been introduced. Gross CO_2 flux is related to a linear

equation based on air temperature. According to the literature the values for b_0 varies between -21 and -173, and t varies between 17.9 and -5.7 (Nykänen *et al.* (2003), however using an iterative solving solution b_0 became 0.196 and t became $4.39x10^{-4}$. These values are not important because using the study of predicting gross fluxes in the earlier part of this chapter it has been found the Lloyd and Taylor (Equation 2.vi) is a better predictor of gross flux for the collars over time.

Using the Nykänen model of net CO_2, and substituting the Lloyd and Taylor equation and regressing the predicted data for net fluxes using equation 2.ix against the measure net flux showed that the equation accounted for 14.02% of the variance of the data (P = 0.001), which is a poorer fit compared to equation 2.viii. Therefore equation 2.viii will be used to predict the carbon budget for the field site.

2.4.5.3. Gaseous Carbon Budget

There are several different methods of estimating the CO_2 budget for the field site for both gross and net fluxes. The first is a simple averaging of the gross and net fluxes from the measured data, and multiplying these values by the number of hours in a year to give a total export of carbon – see Table 2.8.

Collar Number	Carbon Export (Tonnes C $Km^{-2}year^{-1}$)	Flux type (Net, Gross)
1	22.66	Net
2	182.99	Gross
3	92.17	Net
4	182.59	Gross
5	-12.37	Net
6	182.59	Gross
7	44.50	Net
8	208.78	Gross

Table 2.8 Averaged measured CO_2 fluxes multiplied by the number of hours in a year

As can be seen (Table 2.8) collar 5 is the only net sink of carbon, where a carbon sink is defined as negative. All the other collars are a net source of carbon, where a carbon source is defined as positive. To calculate the average carbon budget for the site using Table 2.8 an average of the net fluxes was calculated to give an average CO_2 source of 36.725 tonnes C $Km^{-2}year^{-1}$. As averaging the values over time will bias the results in favour of the season when most of the measured flux values (Net and gross) were collected, in this case autumn, winter and spring, this will bias the net fluxes of CO_2 by having fewer measures of net CO_2 at high PAR values during summer. The results will also bias the gross fluxes of CO_2 from the site as gross fluxes should be higher in summer months, due to high soil temperatures (See section 2.4.5.1 for a discussion on driver variables of gross flux). This should lead to an overall biasing of the results with lower gross flux values and lower net flux values, assuming that CO_2 net and gross flux are

related to PAR and soil temperature and soil temperature respectively.

The second method for calculating the carbon flux for the site takes into account fewer measurements during summer months, by assuming that there is a linear change of CO_2 readings between each measurement of which the rate of change of CO_2 flux is even spread over time, this should give an even distribution of CO_2 measurements throughout the year.

Collar Number	Carbon Export (Tonnes C Km^{-2} $year^{-1}$)	Flux type (Net, Gross)
1	23.42	Net
2	220.40	Gross
3	89.94	Net
4	182.82	Gross
5	-92.98	Net
6	251.52	Gross
7	50.42	Net
8	230.66	Gross

Table 2.9 Yearly Carbon fluxes assuming linear change between measured readings

As can be seen from Table 2.9 the gross flux estimates are higher than averaging all the measured gross fluxes and multiplying by the number of hours in a year. This was expected as gross fluxes are higher in summer when fewer readings were taken; assuming

linear change between the readings over time should reduce this error. Averaging the net fluxes to give an average carbon export number for the site gives a value of 17.699 tonnes carbon $Km^{-2}year^{-1}$, which is smaller than previously calculated for averaged flux readings. The problem with this approach is that no diurnal variation has been accounted for in either gross flux data or net flux data. The only way to take account of this variation is to model net and gross CO_2 over the year in relation to measured driving variables, as no time course of flux readings over a day was taken.

The third and final method for calculating the carbon budget for the site is a different approach and does not use any of the actual measured flux results and predicts each flux reading using soil, PAR values, and the equations discussed in sections 2.4.5.1, and 2.4.5.2. Using equation 2.viii to predict net flux and equation 2.vi to predict gross fluxes, and using the 15 minute data sets for soil temperature and PAR levels as the driving variables the overall fluxes for the site can be calculated. Within this method there are two different measures of GP_{max} (defined by:- equation 2.viii), where one is a theoretical GP_{max} defined by a hyperbola relation between net flux and PAR, and the other GP_{max} is a measured value of the maximum amount of CO_2 taken up by each individual collar. Using the experimentally defined GP_{max} for each collar gives the following calculations of net and gross flux:-

Collar Number	Carbon Export (Tonnes C Km-2 year-1)	Flux type (Net, Gross)
1	-13.36	Net
2	154.98	Gross
3	-29.43	Net
4	135.91	Gross
5	-34.62	Net
6	226.47	Gross
7	148.33	Net
8	243.26	Gross

Table 2.10 Predicted net and gross CO_2 flux based upon experimentally defined GP_{max}

As can be seen from Table 2.10, most of the collars are now a net sink of carbon, and the overall carbon flux from the site is 17.73 tC $Km^{-2}a^{-1}$. This is a similar value to predicting the carbon flux from the site assuming a linear change in CO_2 flux between the measured net flux readings. Predicting net flux using GP_{max} defined by the hyperbola equation gives different flux readings, which affects the overall estimate of carbon flux from the site:-

Collar Number	Carbon Export (tC $Km^{-2}a^{-1}$)	Flux type (Net, Gross)
1	30.83	Net
2	154.98	Gross
3	79.15	Net
4	134.91	Gross
5	101.09	Net
6	226.47	Gross
7	179.36	Net
8	243.26	Gross

Table 2.11 Hyperbola defined GP_{max} and predicted net and gross CO_2 flux.

As can be seen from Table 2.11 using a hyperbola defined GP_{max} calculates that all the collars are sources of carbon, with an overall carbon loss of 97.61 tC Km^{-2} a^{-1}. To represent these fluxes in a more graphic way to compare and contrast the net and gross fluxes from the site a simple bar graph shows these difference in flux calculation:-

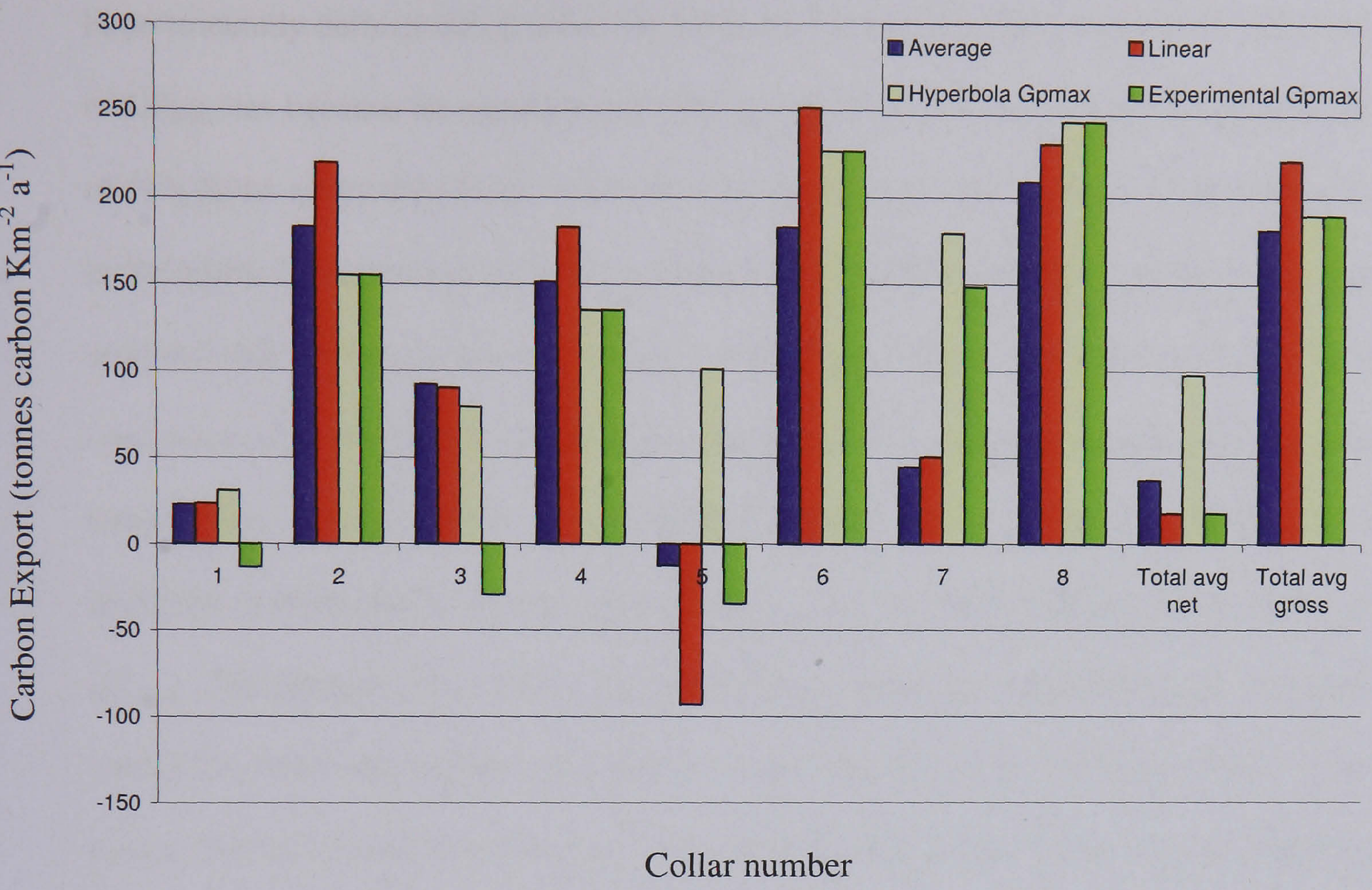

Figure 2.24 Different carbon flux calculations for a year. Where Average = average CO_2 flux multiplied by the number of hours in a year, Linear = an assumed linear relationship of CO_2 over time, Hyperbola GP_{max} = predicting GP_{max} using a hyperbola relationship between net flux and PAR. Experimental = an experimentally define GP_{max} depending on the maximum amount of CO_2 taken up by each collar.

As can be seen from Figure 2.24 there are several different flux calculations results depending on the method used. There are problems with each method:-

The errors associated with averaging CO_2 flux over the year, assuming a linear relationship between each net and gross flux reading for each collar, and the hyperbola method have been discussed previously.

Experimentally defined GP_{max} values do not have the problem that a hyperbola definition of GP_{max} has because an experimental method measures the maximum physical amount of CO_2 taken up by the plants, rather than trying to predict the amount of CO_2 taken up by the plants by measuring different variables. The problem with this method is that it is unlikely that measurements of primary productivity fluxes were taken at optimum conditions of all the factors affecting the amount of CO_2 taken up (Values such as; soil temperature, soil moisture, PAR, atmospheric pressure, and wind speed.), therefore it is likely the experimentally defined values of GP_{max} are not the actual maximum values of GP_{max}. The implication of this is that if the GP_{max} values are underestimated, the plants within the collars are capable of taking up more CO_2 than experimentally defined; this means that the overall CO_2 flux may be underestimated, and the field site could take up more CO_2 than predicted. Therefore, this could mean that overall the total carbon flux from the field site is underestimated. As the estimates of the overall carbon flux for the field site range from 17.73 to 97.61 tC $Km^{-2}a^{-1}$, and as these values are probably an overestimation of the carbon flux from the field site it would suggest that the field site is either a small sink of carbon or a small source of carbon. The best flux export figure for the field site is 17.7 tC $Km^{-2}a^{-1}$, as two of the predictive methods (Linear and GP_{max} experimentally defined) gave a similar answer and although not perfect answers, they are a best estimation value.

2.5. Discussion

The carbon stores at the Hexhamshire common field site are still vast. The peat was core

to depths of over a metre and bedrock was not reached. This means that there are many hundreds of tones of carbon at the Hexhamshire common field site, and if scaled up over all the upland peat in the UK this equates to a significant store of carbon. As the results have shown, the peat has turned from a sink to a source. This will have major implications on the planet's carbon cycles if more and more peat bogs dry out and start fluxing huge amounts of carbon. This loss is slightly offset against the reduction of methane fluxes into the atmosphere because methane is a more effective greenhouse gas, but the small quantities of methane no longer being released will do little to offset the increasing amounts of carbon dioxide being released into the atmosphere.

2.5.1. Seasonal Treatment

In the short time frame of this project, it does not appear that a water table treatment effect has any relationship to gross, net or primary productivity fluxes this is the conclusion found by Nieveen et al (2005) that there was no relationship between the depth to water table or soil moisture content and soil CO_2 fluxes. At the Hexhamshire common site the water table does vary over time with a distinct seasonal variation however this seasonal variation does not account for any statistical variation in the flux values. Changes in water table depth are closely related to the amount of rainfall, as peat is very flashy, with rainfall water almost immediately entering the hydrological pathways of the peat. Any water that does enter the peat is released quickly from the edges of the peat next to the grips, and more slowly from the middle of the peat. Another property of peat that affects the hydrological cycle of upland peat is peat is either extremely

hydrophilic, when wet, or hydrophobic when allowed to dry, this means that if peat is allowed to dry out then it can take a long time to rewet. This has implications for the hydrological cycle of the peat, which could be a possible impact of global warming, and the upper surface of the peat becoming hydrophobic, this will act as an impermeable barrier to water and will lead to increased overland flow, which will further drain peat and drying it to a greater extent. This will also lead to greater volume of water leaving the peat during a rainfall event. According to literature (Dirks *et al* 2000; Lloyd 2006) as long as peat is kept wet but with a low water table, CO_2 will continue to flux from the peat surface. However if peat is severely dried the microbe population will lower and the amount of CO_2 produced will be reduced (Wessolek *et al.,* 2002). The implications of this are important because with drier summers and wetter winters predicted for the UK (Hulme *et al.,* 2002) peat will flux CO_2 during the winter and spring months, but the CO_2 flux may become restricted by soil moisture availability during summer months, especially at high temperatures. Therefore peat may actually release less carbon than a purely temperature modelled CO_2 response to climate change. Another negative effect of severely drying peat is the increased risk of wildfire. If peat is kept wet then the probability of a wildfire event is decreased, but dry peat burns very easily, and there is the potential to release a large amount of carbon into the atmosphere in a very short space of time. In the long term, restoring the water table should have an effect on the amount of carbon dioxide released from the peat; however the timescale over which this study is taken is too short to see these changes in the data.

When considering remediation of a site it is important to consider the original substrate

quality and the quality of the substrate at present. The substrate quality at the Hexhamshire common site cannot have been disturbed too much during the digging of the grips, because the main peat forming plant – S*phagnum*, has begun to colonise the open water in the blocked grips, and still remains in large patches at the peat surface in the wetter areas. This is significant because if *Sphagnum* was unable to colonise open water, this would lead to increased evaporation from the water surface, and maintain high runoff levels. Ultimately, the water would dry out and then there would be no opportunity for the peat to restore to its natural condition. The *Sphagnum* could help restore the peat grips much quicker than by infilling the grips with plant growth as the *Sphagnum* will precipitate any large carbon particles within the grip by the *Sphagnum* leaf system (as *Sphagnum* has no roots), by reducing the water flow rate. *Sphagnum* has incredible water retention properties, and can actually draw the water table up and helps maintain an anaerobic environment, which should reduce the amount of carbon released from the peat surface. From a visual survey of the vegetation types at the Hexhamshire Common field site it is noted that where *Sphagnum* moss occurs at the peat surface it occurs near to the wetter areas of the peat surface as measured by the piezometer wells.

The greater the aerobic volume of the peat the greater the amount of CO_2 produced as CO_2 is mainly produced in aerobic zones or zones that have a supply of oxygen. Therefore during a period when there was a sharp drop in water table then it would be expected that there would be a corresponding increase in the amount of CO_2 produced, however no responding increase can be seen (Figure 2.10). In fact, the opposite can be seen during a very wet summer when the water levels rose to similar levels found in

winter, the CO_2 fluxes were at there highest rather than being lowered due to the high water table. This led to the conclusion that there is no short-term water table effect upon CO_2 fluxes. This does not mean that there is no water table effect but that any water table effect is on a longer time scale than the time scale of this project, or any effects are being masked by larger driver effects such as soil temperature. There could be several reasons for this decoupling of the water table from the CO_2 flux levels. The first is that the peat could remain aerobic as the water table levels increase by trapping pockets of oxygen which is then used by the microbes until the peat become aerobic again. The second is that the plants could be providing oxygen to the substrate via the roots below the water table surface. It is well documented that this is an important process in transporting methane to the surface (Whiting *et al.,* 1992, Morrissey *et al.,* 1993, Bubier *et al.,* 1994, Chanton *et al.,* 1995, Schimel, 1995), but there is little documentation as to whether this process can happen in reverse. The third is that as the water table decreases in depth i.e. the depth becomes shallower, then this will act as a flushing effect, pushing CO_2 upwards and out of the peat as the water table depth decreases. This would mean that although there would be no increase in the amount of CO_2 produced it would appear that CO_2 is still being produced at the same or higher rate as at a greater water table depth, however it would be seen that the CO_2 production would decrease as the water table dropped to pre rainfall levels, and this is not seen. An alternative theory is that the greater the water table depth the greater the amount of methane oxidation will occur so it would appear that the greater the water table dept the greater the amount of CO_2 would appear to being produced. However, CH_4 occurs in such small concentrations from the peat surface it would not explain any variance in the amount of CO_2 produced if there was a relationship

between water table depth and the amount of CO_2 produced. Another possibility is that the maximum CO_2 production occurs at a given soil moisture content. This would manifest itself in the data as a lower CO_2 fluxes above this theoretical soil moisture limit, producing a gradient of CO_2 flux down and slightly below the water table depth limit, due to oxygen diffusion. When the water table is drawn down, this again would act to depress the CO_2 fluxes along a gradient to the surface where CO_2 flux is being inhibited by a lack of soil moisture. This would act to reduce the effect of water table depth on the CO_2 flux as the relationship between these two variables is not linear or log linear. In truth it could be any of these factors or any combination to a lesser or greater extent. Without a more detailed investigation, the only conclusion that can be drawn from this study is that water table has no statistically significant affect on the amount of CO_2 produced by the peat.

2.5.2. Sink or Source?

Taking all the measured data and predicting whether the field site is a sink or source gives a bias view as to whether the field site is still taking up carbon because the measurements were collected on specific days and at similar time of the day, which was often not at the peak time of either respiration or photosynthesis. In addition, there were fewer readings taken over the summer months in accordance with the land owners wishes, and this would bias the data to favour of the winter months when little or no photosynthesis occur. Although few readings were taken in the dark and compared to readings taken during daylight hours, much of the respiration will occur during these

hours. Therefore, to get an accurate measure of the amount of carbon lost or gained by the field site a more accurate measure will be obtained when considering the modelled CO_2 fluxes. These fluxes were modelled on a fifteen minute data sets of soil, air and water temperature, and PAR. Looking at the raw 4 second data files for the IRGA, there are definite responses in CO_2 concentration levels to changes in light levels when events such as the sun coming out from behind a cloud (Figure 2.25).

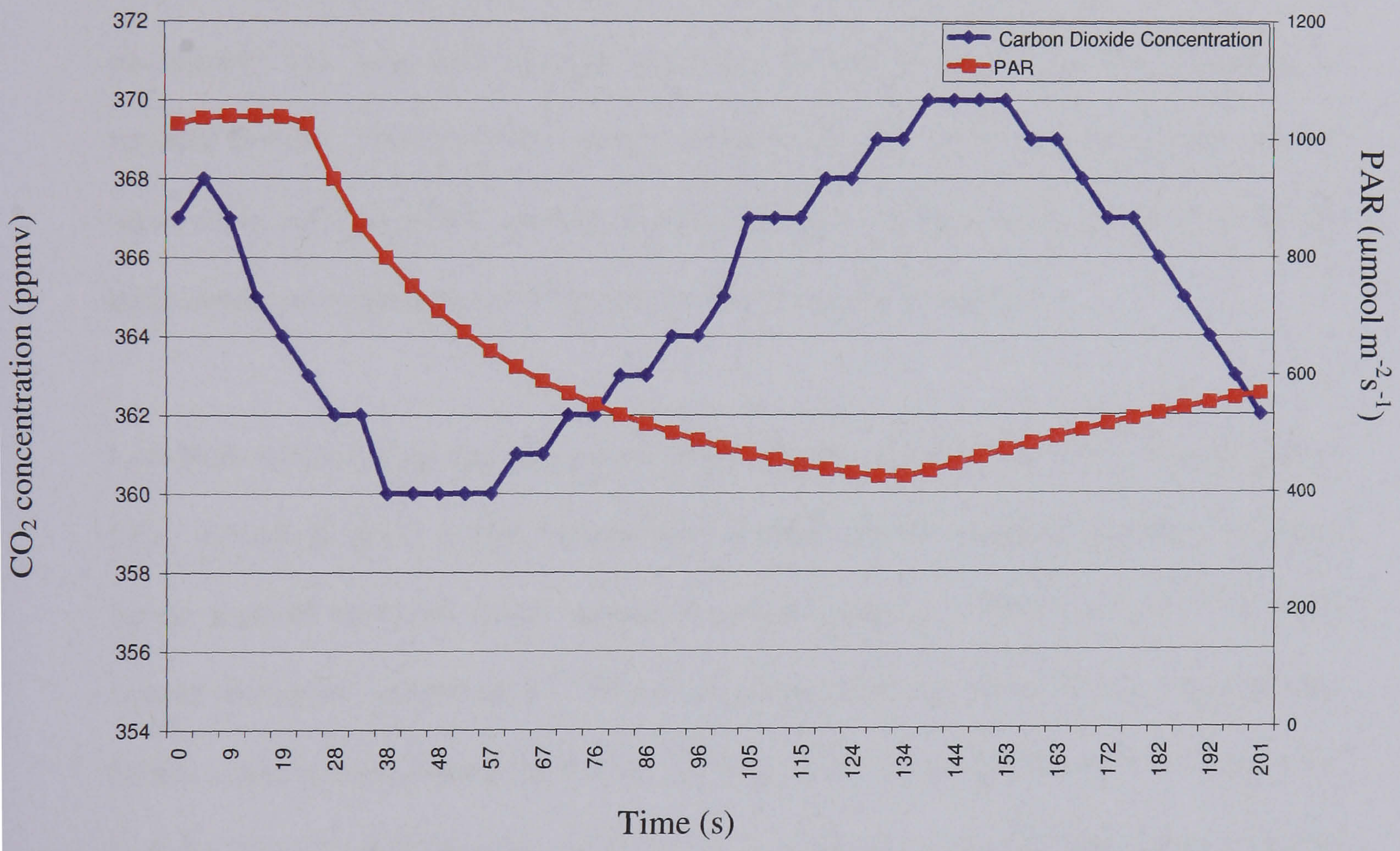

Figure 2.25 Changing CO_2 concentration within flux chamber due to PAR levels

It was assumed that when there was zero PAR, NEE was equal to R. With the result of a release of 17.7 tC $Km^{-2}a^{-1}$, confirms that the field site is a source of carbon.

2.5.3. How representative are these results?

These results have been collected and modelled over a year, and because this field site is part of an on going project there is more than one year of some of the environmental data such as soil air and water temperatures, rainfall, and flow. The data specifically collect for this project such as PAR and water table depth is only available on the same time scale as the project. Comparison with previous years data shows that 2003/2004 was a particularly wet year with August being the wettest august on record according to national figures. This could be a reason why this project found no relationship between water table and flux levels, because in other studies which studied typical years, water table depths are related to soil temperature due to seasonal variation.

Literature studies of upland ecosystems show a range of values for the release/uptake of CO_2. Trumbore *et al.,* (1999) found, using a closed chamber method, that for a series of boreal wetland sites the values ranged from an uptake of -164.15 gC $m^{-2}a^{-1}$ to a net carbon release of 2.65 gC $m^{-2}a^{-1}$. Where the range of values comes from a range of sites from a collapsed bog (Released 2.65 gC $m^{-2}a^{-1}$), a poor fen (Sequestered -111.19 gC $m^{-2}a^{-1}$) and a rich fen (Sequestered -15.24 gC $m^{-2}a^{-1}$) where an intermediate fen sequestered the maximum amount of carbon (-164.15 gC $m^{-2}a^{-1}$). When compared to the overall release of 17.73 gC $m^{-2}a^{-1}$ from this project it shows that a drained and restored site releases more carbon than a pristine wetland site. A similar study by Roehm *et al.,* (2003) found that the annual carbon budget for a northern bog was an uptake of -76 gC $m^{-2}a^{-1}$. Another study by Nykanen *et al* (2003) showed a subarctic palsa mire sequestered

on average -36.9 to -138.6 gC $m^{-2}a^{-1}$. Again, both of these studies have a much larger uptake of carbon than the release of 17.73 gC $m^{-2}a^{-1}$ found in this project. A study by Nieveen *et al* (1998) using an eddy covariance method calculated a net release of carbon of 97 gC $m^{-2}a^{-1}$, which is a much larger value of carbon release than calculated in this project. The method used by Nieveen *et al.*, (1998) was similar in method to this study as opposed to the other studies mentioned above (Trumbore *et al.*, 1999, and Roehm *et al.*, 2003) as this peat land was drained and then the drainage channels blocked to raise the water table. A further study by Oechel *et al* (2000) found from a long term study of carbon release from Alaskan arctic tundra that pre 1976 levels artic tundra sites were a sink of -25 gC $m^{-2}a^{-1}$ for a wet sedge ecosystem while moist tussock tundra ecosystems were reported to be net sinks of 120 gC $m^{-2}a^{-1}$ with an average ambient temperature 0.6 - 0.7°C cooler than the overall average temperature for the sample period. During the mid 80's and early 90's the wet sedge was measured to be a source of 25 gC $m^{-2}a^{-1}$, whilst the moist tussocks lost between 50 and 450 gC $m^{-2}a^{-1}$ when the average temperature was 0.5°C warmer than the overall average temperature. Having turned from a sink to a source, it was noted by Oechel that, post 1994 the summer uptake rates increased, and summer source rates decreased making the site a net summer sink of carbon. Oechel then hypothesised that the ecosystem will ultimately become a sink again, with results perhaps not being manifest for decades.

Other studies have completed the gross carbon cycle for upland systems. A study by Raich *et al.*, (1992) compared the gross release of carbon from many different ecosystems. Looking at the released carbon collated in the Northern Bogs and Mires

sections shows that there is a range of gross carbon released ranging from 7 gC $m^{-2}a^{-1}$ to 180 gC $m^{-2}a^{-1}$ of which the average was 87.58 gC $m^{-2}a^{-1}$. In this study the gross release of carbon is greater than the largest amount from the Raich study, 180 gC $m^{-2}a^{-1}$ where this study had an average release of 189.906 gC $m^{-2}a^{-1}$. Chapman (1996) reported gross release values ranging between 6.8 mgC $m^{-2}h^{-1}$ to 169 mgC $m^{-2}h^{-1}$, whereas this study found gross export values between 0.01 mgC $m^{-2}h^{-1}$ and 316.746 mgC $m^{-2}h^{-1}$. From these values it can be seen that this study had a greater range of values than the Chapman study. The localities for the Chapman study are located between the Shetland Islands and Aberdeen. The Shetland Islands are located over 400 miles North of this field sites in this study, and the Aberdeen field sites are located 175 miles North of the Hexhamshire Common field site. This increase in latitude will affect the average temperature of the field site. Chapman reported accumulated temperatures between 740 and 1020°C d^{-1} whilst at the Hexhamshire common field site accumulated temperatures for 2003 were 2387.54°C d^{-1} for soil temperature and 2513.59°C d^{-1} for air temperature. As can be seen from these results the Hexhamshire common site is much warmer and therefore higher flux values would be expected.

From these results of carbon budgets and gross carbon fluxes from upland sites it can be said that the Hexhamshire Common field site is source of carbon, as other field sites have shown to be. The magnitude at which the Hexhamshire Common field site is releasing carbon is less than other field sites overall. For gross fluxes, it can be said that the Hexhamshire Common field site is releasing more carbon than a series of other upland sites (Raich *et al.*, 1992). The implications of this are that this drained upland peat is

releasing more carbon that other pristine upland sites as found by Trumbore *et al.*, (1999), however when compared to other drained sites (Nieveen *et al.*, 1998), or sites that have a lower water table due to drying effects (Oechel *et al.*, 2000) the fluxes are lower or comparable.

Methane released 1.38 tC $Km^{-2}a^{-1}$ or 1.38 gC $m^{-2}a^{-1}$ from the Hexhamshire common field site. Compared with literature values from Nykänen *et al.*, (2003), CH_4 release was between 1.0 to 24.7 gC $m^{-2}a^{-1}$. As can be seen from the above results the amount of CH_4 released in this project is lower than the amount of CH_4 release in the Nykänen project. Hughes *et al.*, (1999) reported maximum methane emission from a control field site of 8.75 mgC $m^{-2}h^{-1}$, compared to 2.81 mgC $m^{-2}h^{-1}$ for the experimental wetland with an increased water table depth, which is three times more than the emissions from the Hexhamshire Common field site. The maximum CH_4 release values from the Hexhamshire common field site were 1.1 mgC $m^{-2}h^{-1}$. Macdonald *et al.*, (1998) reported mean CH_4 flux values from a field site at Loch More, Caithness, Scotland of 0.21 mgC $m^{-2}h^{-1}$ for a field site with similar vegetation to the Hexhamshire Common field site (Eriophorum spp., *Sphagnum* spp., and Calluna Vulgaris). When recalculated; CH_4 fluxes in mgCH_4 $m^{-2}h^{-1}$ are 0.28 mgCH_4 $m^{-2}h^{-1}$. For the Hexhamshire Common field site the average flux is 0.21 mgCH_4 $m^{-2}h^{-1}$. As can be seen from these results these figures are comparable with each other. The implications of this are that as the field site are located in the same country, although separated by over a hundred miles the methane fluxes are comparable and methane has been proven to have little relation to soil temperature, which would be the main effect of increased latitude. When these two

results (Hexhamshire Common and Caithness) are compared to another study of methane flux by Nakano *et al.*, (1999) it can be seen that the CH_4 fluxes measured were much higher at 1.45 mgC $m^{-2}h^{-1}$ from one site whilst another site had fluxes of 8.78 mgC $m^{-2}h^{-1}$. Van Den Pol-Van Dasselaar *et al.*, (2002), reported average annual export values for CH_4 on wet grasslands on peat in the Netherlands of 0.26 mgC $m^{-2}h^{-1}$ to 3.16 mgC $m^{-2}h^{-1}$. These values, when compared to the values from the Hexhamshire Common site (0.16 mgC $m^{-2}h^{-1}$) are higher from one of the field sites and much higher from the other.

The implications of this are that these CH_4 fluxes are comparable to other drained upland systems, whilst being incomparable with other sites. There appears to be large differences in the amount of CH_4 fluxing from the peat surface, which does not appear to be explained by drainage, temperature, or other readily available environmentally measured factors.

2.5.4. Problems with the data and experimental design

The main problem with the experimental design was the time course of the experiment, the readings could have been taken over a longer time course to find if there was a statistical relationship between CO_2 flux and water table depth. The same is true with CH_4. This gas could have been measured more frequently to give a better idea of the flux relationship between CO_2 and CH_4. Another problem with the data was the use of two different methods of measuring CO_2 fluxes. Statistically the gross flux collars are the

same, the problem lies with the net flux collars. The design of the chambers with a clear acrylic top and opaque walls reduced the amount of PAR into the chamber to a much greater extent than purpose build acrylic chamber. A series of comparison readings were taken with both chamber types on the same day to try to find a calibration between the chamber types, unfortunately this was not possible. This led to a modelled net flux of CO_2 based upon PAR and soil temperature for a portion of the year, using the fluxes measured with the original acrylic chamber and comparing the modelled and actual data to find the best fit. Another problem with collecting the data was the interaction with the peat by walking across the peat to the collars. Walking across the peat will cause it to release bubbles of CO_2 and CH_4 by small compactions of the peat. This was minimised by walking on in the same place every time readings were taken and a length of carpet across the peat was used to spread weight. A better approach would have been to construct a board walk system, but this was not possible due to land owners wishes. Some of the water table readings were not accurate because of the way they were measured. Water table depth was measured using a piezometer well with a pressure transducer at the bottom of the well which measured the pressure of the water above it. This value was then calibrated against manual hand readings of water table depth. The problem with the data occurs during cold periods when the water in the piezometer wells would freeze slightly; this would increase the pressure on the pressure transducer as the water expanded as it froze, giving negative water table depth i.e. the water table was above the surface of the peat.

2.6. Conclusions

In this study, it has been concluded that there is no relationship between the average yearly gross CO_2 flux for each collar when compared to the yearly average water table depth for each collar. In addition, there was no relationship found between a plot of gross CO_2 flux and water table depth for each flux reading. A slight visual relationship could be seen between water table depth and CO_2 flux with fluxes generally being higher when water table depths were lower and correspondingly lower when water table depths were higher. A statistical analysis of the gross CO_2 flux data revealed no relationship between water table depth and gross CO_2 flux. Therefore, it can be said that there is no relationship between water table depth and gross CO_2 flux over a 12-month period.

Both net CO_2 flux and primary productivity fluxes showed no relationship to water table depth, as with gross CO_2 fluxes, for; yearly averaged values of net flux and water table depth, no linear relationship between a plot of the individual net and primary productivity fluxes and their respective water table depths. There was also no visual relationship between net and primary productivity fluxes over time and water table depth over time. As with gross CO_2 flux, a statistical analysis of net and primary productivity fluxes revealed no relationship. Therefore, there is no relationship between gross, net and primary productivity CO_2 fluxes with water table depth.

Looking at the CH_4 fluxes in relation to water table showed that there was no relation between yearly average CH_4 fluxes for each collar and yearly averaged water table depth.

A plot of CH_4 flux against water table depth showed that there could be a slight negative relationship between water table depth and CH_4 fluxes, as CH_4 fluxes were higher when water table depth was shallower, and CH_4 fluxes were lower when water table depth was deeper. This relationship was discounted as a statistical analysis of CH_4 fluxes and suggested driver variables showed that water table depth was insignificant in relation to the concentration of CH_4 released.

In defining the effects of seasonal climate variation on CH_4 fluxes it was found that none of the variables (Soil, air and water temperature, water table depth, PAR, collar number, season, logged Soil, air and water temperature, logged water table depth, and logged PAR) were statistically significant in relation to the magnitude of CH_4 released.

Although statistically there is no relationship between water table depth or season with CO_2 flux, it is logical to assume that there is an effect on the relative magnitude of the CO_2 flux by both season and water table depth. To answer the question of which has the larger effect the relative contribution of season or treatment to CO_2 flux was determined by partial correlation. It was found that, for gross flux, season had a greater effect on the magnitude of CO_2 flux released from the peat surface than water table depth. For net flux it was found that depth to water table had a greater effect on the fluxes than season, the same was true for primary productivity fluxes. A conclusion that can be drawn from this is that the water table depth is affecting the plants on the peat surface, which in turn is affecting the amount of CO_2 the plants are taking up.

Investigating the effects of seasonal climate variation on CO_2 and calculating a carbon budget for the field site led to the definition of the important variables contributing to the relative magnitude of CO_2 flux. For gross flux, the important variables were soil temperature and collar number. This concludes that the gross flux collars are statistically different from each other, and were affected by seasonal changes in soil temperature. A literature review revealed that there were three main methods of predicting CO_2 flux; a linear relationship between soil temperature, an Arrhenius relationship between soil temperature, and an equation defined by Lloyd and Taylor (1994). From these three methods for modelling CO_2 flux it was found that the Lloyd and Taylor (1994) equation accounted for the greatest proportion of the variation within the gross CO_2 flux data. As the collars were statistically different from each other, this was accounted for by defining R_{10} values for each collar. It was found that the best way to predict the R_{10} values for this field site was to iteratively find the best R_{10} value for each flux reading, and average these values for each collar. It was also found that R_{10} values for a site could be found without experimentally defining the R_{10} value by substituting the Lloyd and Taylor equation into the Q_{10} equation, which cancelled the R_{10} values from the Lloyd and Taylor equation and defined R_{10} values based on different intervals.

When defining the relative magnitude of effect of seasonal climate variations on net CO_2 data it was concluded that the important variables which contributed to the magnitude of the net CO_2 flux were air temperature, PAR, and Log PAR. From a literature review it was found that there were two different equations where used to model net CO_2 flux. The first equation was from Bubier (1998) and the second was from Nykänen (2003), it

was found that the Bubier equation (1998) accounted for the greatest proportion of variability of the measure net flux data. From this modelled data it was concluded that the field site is a net source of carbon of 17.73 tonnes C $Km^{-2}a^{-1}$.

3. Third Chapter: Dissolved Inorganic Carbon

This chapter determines the dissolved CO_2 concentration in drainage water from an upland peat. This chapter then examines the relationship between dissolved inorganic carbon (DIC) and the carbon stores from the same upland peat, and attempts to improve a best fit respiration model.

3.1. Introduction

3.1.1. Excess CO_2 dissolved in drainage water from an upland peat.

Dissolved CO_2 in drainage waters from an upland peat is typically supersaturated, and has partial pressures of CO_2 many times in excess of atmosphere equilibrium (Dawson *et al.,* 1995, 2002; Cole *et al.,* 1994; Kling *et al.,* 1991; Hamilton *et al.,* 1994; Hope *et al.,* 2001;). As CO_2 is normally in excess of atmospheric CO_2 it will flux into the atmosphere, and thus these surface waters can act as significant conduits of carbon to the atmosphere (Hamilton *et al.,* 1994; Kling *et al.,* 1991; Cole *et al.,* 1994; Skiba *et al.,* 1991; Dawson *et al.,* 1995), where small drainage systems of upland peat are the first entry point of excess CO_2 from within upland peat into the drainage system (Jones *et al.,* 1998). The exchange of CO_2 between surface water and the atmosphere can be a

significant source or sink of CO_2 to the atmosphere on a global or regional scale (Sarmiento *et al* 1992; Quay *et al.,* 1992; Kling *et al.,* 1991; Cole *et al.,* 1994). Excess CO_2 in upland waters will affect the downstream chemistry by increasing the buffering capacity of the river. This has impacts on water treatment works, where an increase in buffering capacity would require changes to the water treatment process such as adding lime to neutralise this buffering capacity thus making water treatment more expensive (Guldner *et al.* 1994; Fleck *et al.,* 2004).

Dissolved CO_2, produce by in-stream processes, is typically low suggesting that the major source of dissolved CO_2 is ground or soil waters (Worrall *et al.,* 2005; Kling *et al.,* 1992). Carbon dioxide dissolved in groundwater is produced in the shallow aerobic soils, and is regulated by available nutrients, temperature, organic matter quantity, and quality and oxygen (Yavitt *et al.,* 1987). Dissolved CO_2 in stream waters which is in excess of the concentration of CO_2 of the atmosphere is called excess partial pressure of CO_2 ($EpCO_2$) (Worrall *et al.,* 2005). Variability in excess partial pressure of CO_2 between streams should reflect differences in soil respiration in different catchments and potentially can be used to characterise variations in soil metabolic activity and to test hypotheses about soil CO_2 production (Jones *et al.,* 1998).

3.1.2. Excess CO_2 in drainage waters

Carbon dioxide is produced within the soil pore spaces and the amount of CO_2 produced has been linked to the aerobic volume of the peat (Cresser *et al.,* 1987, Skiba *et al.,*

1991). The greater the volume of aerobic peat the greater the amount of CO_2 produced (Van Huissteden *et al.*, 2006), and therefore, the greater the amount of CO_2 dissolved into the soil pore waters (Dawson *et al.*, 2002). This soil pore water is then either flushed or flows into the drainage system (Clow *et al.*, 1996), often in excess of the CO_2 concentration in the atmosphere, leading to CO_2 fluxing directly from the drainage surface into the atmosphere (Pinol *et al.*, 1992).

3.1.3. Sources of dissolved CO_2 from upland peat in drainage waters

There are three main source of CO_2 that contribute to CO_2 in drainage waters. The first is from the atmosphere its self, which will equilibrate with all open waters. The second source of CO_2 into drainage waters is from geological sources (Cole 1998, Wetzel 1983, Wetzel *et al.*, 1991). If the underlying geology of an area is carbonate based then, as the carbonate weathers, calcium carbonate ($CaCO_3$) will dissolve into the drainage waters (Worrall *et al.*, 2005, 2003). The third and final source of CO_2 is from the peat itself, where CO_2 has been produced within the matrix of the peat, and dissolved into the soil pore waters and then either flushed or flows, due to ground water movement, into the drainage system (Cresser *et al.*, 1987, Skiba *et al.*, 1991).

3.1.4. Completing the dissolved carbon budget for an upland peat

To complete the dissolved carbon budget for an acidic upland peat catchment, the amount of CO_2 dissolving into drainage waters in excess of the amount of CO_2 already dissolved in the sample water due to equilibrium with the atmosphere, needs to be found. Ideally, this would be done by continuous measurements of the partial pressure of CO_2 within a water sample, however this is often unrealistic due to the methods of calculating dissolved CO_2 in solution. Therefore, to find the amount of dissolved CO_2 leaving the peat, careful modelling needs to be done to determined the speciation of different elements within the river samples. Once the different species within the complex river system have been constrained, the excess concentration of CO_2 dissolved in the river waters can be calculated. Measurements of $EpCO_2$ are defined as the excess partial pressure of CO_2 dissolved in a drainage system compared to if the system is in equilibrium with the atmosphere (Hope *et al.,* 1995). To measure these different components of the speciation model, several basic measurements need to be taken these are; pH, alkalinity or acidity, total calcium concentration (mg l^{-1}), total aluminium concentration (mg l^{-1}), dissolved organic carbon (DOC), and water temperature (K). This information can be used to construct a speciation model, which can be used to predict the concentrations of the different ions in the sample from which the excess partial pressure of CO_2 in the sample can be found. Depending upon the pH of the samples either acidity or alkalinity is measured. If the pH of the sample is below 4.5 then acidity is measured, if the pH is above 4.5 the alkalinity is measured (Stumm and Morgan 1981; Butler 1982).

Once the concentration of the excess partial pressure of CO_2 within a river system, has been calculated, the aim is often to calculate the total dissolved carbon portion of the carbon cycle with the aim of completing the total carbon budget for a site, with respect to CO_2. It is logical to hypothesize that at any one point in time there is a fixed amount of CO_2 being produced within the peat, with the concentration of CO_2 produced depending on driver functions such as soil temperature, and the volume of aerobic peat. Different hydrological conditions will determine what proportion of the total CO_2 concentration produced will partition to the atmosphere or as dissolved carbon in the drainage system, thus an interpolation method can be applied to find the total carbon budget.

3.2. Objectives

The objectives of this study are:-

1. To determine the dissolved gaseous concentration of CO_2.

2. To determine what controls affect the concentration of dissolved CO_2 in peat drainage waters.

3. To determine the combined gaseous carbon budget for the Hexhamshire Common field site?

4. To determine whether the main sources of CO_2 are from either geological or peat based sources.

5. To determine whether there is a constant amount of CO_2 produced based on driver variables

6. To improve the prediction of total CO_2 production for peat

3.3. Methods

3.3.1. Site descriptions and layout

In this project there are three different sites each of which has a different treatment. The first site, called Hexhamshire Common, has already been described in chapter 2, section 2.3.1. In addition to the description in chapter 2 section 2.3.1 the Hexhamshire Common field site has three drainage ditches (referred to as: Hex 1, Hex 2, and Hex 3), locally called grips. Two grips were blocked using a peat dam method which involved taking a cut of peat from the drainage walls and using this to block the drainage channel, these grips were labelled Hex 1 and Hex 3. The third grip was allowed to drain freely and was labelled Hex 2.

The next study site is located 17.2 km south west of the Hexhamshire Common field site and is located on the northern slope of Cowgreen reservoir, henceforward called Cowgreen (NY 80030 31790) (See Figure 3.1). This is an older gripped site with the grips having a much wider spacing, greater than 20 meters. All of the grips at this site were blocked in 1995. The field site has been classified according the national vegetation classification as an M20b – *Eriophorum vaginatum* blanket mire and raised mire. The main plant species are *Eriophorum vaginatum*, *Polytrichum commune*, with infrequent *Calluna vulgaris*, and *Sphagnum capillifolium*. This site has been degraded from an M19

Calluna vulgaris – Eriophorum vaginatum blanket mire by drainage and grazing.

The third and final site is located approximately 2.12 Km East from the Cowgreen reservoir site, and is situated at the eastern end of the Cowgreen reservoir near the dam, on a small stream in an area called Widdybank Fell (GR NY 81675 30450), henceforward called Widdybank (See Figure 3.1). This is a natural stream and chosen for its pristine condition, and is located in a SSSI site, a short distance from the shores of Cowgreen reservoir. This treatment is called natural in this chapter. The field site has been classified according to the national vegetation classification scheme as an M19 *Calluna vulgaris – Eriophorum vaginatum* blanket mire. The main plant species are; *Eriophorum vaginatium*, *Sphagnum capillifolium*, and *Calluna vulgaris*. The proportion of *Calluna vulgaris* has increased due to burning.

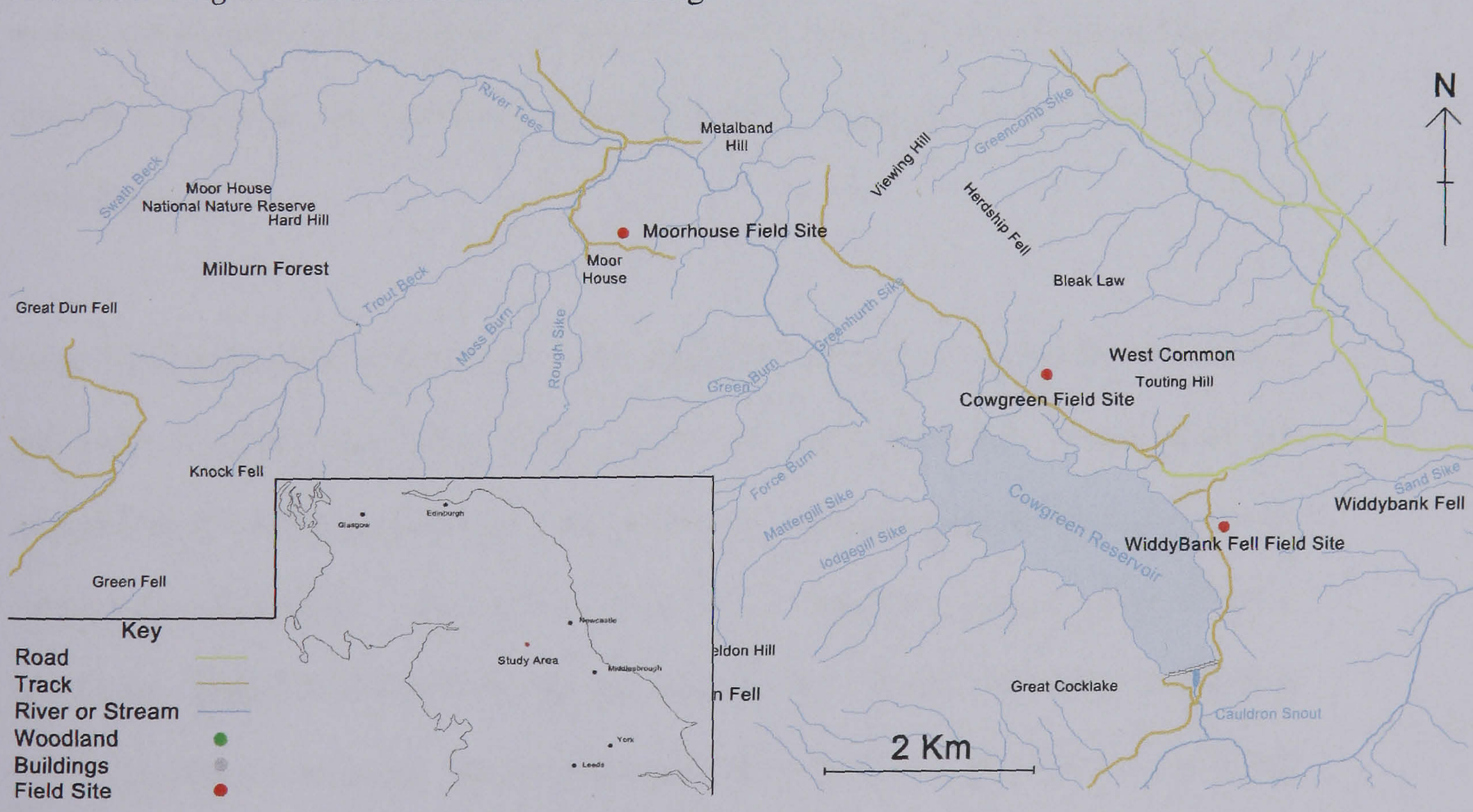

Figure 3.1 Location of Cowgreen, Widdybank Fell and Moor house Field sites

3.3.2. Experimental Design

Water samples were collected on a weekly basis in winter from the 5/11/2003 until the 22/04/2004 and every three weeks in summer from the 13/05/2004 until the 11/08/2004, in accordance with the land owners' wishes, after which the sampling returned to weekly sampling until the 9/12/2004. Five samples were collected from the three different sites covering all five drains. The first was collected from an old blocked grip at the Cowgreen site, and the second was collected from a natural stream at the Widdybank site. The final three sample were collected from two blocked grips and an open grip at Hexhamshire Common. Water samples were collected in 1 litre sample bottles; all of the sample bottles were, whenever possible, sealed under water to prevent any headspace in the bottles. However if the grips had little water in them then the sample bottles were filled as full and as quickly as possible, and then the bottle caps filled with water and fitted as quickly as possible and squeezing the bottle slightly, again, to prevent any headspace from forming.

Once the samples were collected they were analysed the same day in Durham for pH and alkalinity or acidity depending on the sample pH. A small sample was retained for analysis by ICP OES (Inductively Coupled Plasma Optical Emission Spectrometer) for calcium and aluminium. Analysis was performed on unfiltered samples using a Perkin and Elmer Optima 3300 RL ICP-OES machine and ICP Winlab was used for machine control and data processing. Mixed standards for analysis were produced using Romil ICP standards and a serial dilution technique. Standards (including blanks) were run

prior to analysis and the 50 and 25 mg L^{-1} standards were re-analysed as samples approximately every 25 samples as a manual check for drift; all standards were re-analysed at the end of each run (Gibson 2006). Concentrations of DOC were analysed by spectrographically with calibration of this technique by the method of Ohno and Crannell (Gibson 2006).

Gran alkalinity or gran acidity was measured depending upon the pH of the solution, All of the samples, from Hex and Cowgreen had a pH below 4.5, so gran acidity was measured, and for the Widdybank Fell field site the pH was always above 4.5 therefore gran alkalinity was always measured.

Gran acidity was measured using a titrometric method which took 30ml of a sample from one of the field sites and a 0.1 M solution of sodium hydroxide (NaOH) was added drop wise to the solution with phenolphalien being used as an indicator to determine the end point of the reaction. This determined the overall buffering capacity of the solution.

To determine the gran alkalinity for the sample from Widdybank Fell the method was similar to determining the gran acidity of a solution; 30ml of the sample titrated against a 0.1 M solution of hydrochloric acid (HCl), with bromophenol blue being used as an indicator to determine the end point. Methyl orange could also be used as an indicator to determine the end point of the gran alkalinity reaction, but as many of the samples were already brown in colour this interfered, visually, with the end point of the reaction.

3.3.3. Climatic measurements

The site was also monitored for a series of climatic measurements; see chapter 2, section 2.3.4 for a complete list.

3.3.4. Statistical analyses

There were two different statistical analyses performed on the dissolved CO_2 data; multiple linear regression, and analysis of variance (ANOVA).

Multiple linear regression studies the relationship between several independent or predictor variables in relation to a dependent or criterion variable. In this case the criterion variable is a flux estimate which, in the case of this study will be the excess partial pressure of CO_2 in solution per litre of river water per hour. The variables used in the regression were flow, conductivity, sum of the daily rainfall (which is the sum of all the 15 minute rainfall totals for the sample day), and average of the 15 minute rainfall (which is the average amount of rainfall to fall during a 15 minute period on the sample day), season (Where January = 1, and December = 12, and has been transformed via the following equation; $\text{cosine}\left(\left(\frac{(\text{month number} \times \pi)}{12}\right)\right)$, gross gaseous CO_2 flux, net gaseous CO_2 flux, log conductivity, and log flow all the variables were considered at the 95% significance level.

Analysis of covariance was performed using a regression approach. A "Full Rank"

design matrix is formed from the factors and covariates and each response variable is regressed on the columns of the design matrix. In this example, the response variable is the excess partial pressure of CO_2 in solution; the covariates are the terms which are significant in the multiple linear regression study. The study factor is treatment i.e. whether the grip is blocked, unblocked, an old blocked grip, or a natural stream.

3.3.5. Determining a Model for Speciation of acid and alkali stream waters.

This model is based upon the model designed by Neal *et al.,* 1994 & 1998. The basic measurements collected were: the total buffering capacity of the solution, either; alkalinity or acidity, pH, water temperature, total aluminium, calcium and DOC concentrations. The speciation model was based upon the ability of the molecules to dissolve / speciate within the sample and either loose hydrogen ions or gain hydroxide ions.

When the pH of a solution is greater than 5 the appropriate equilibria equations are:-

$$K_H = \frac{[\text{Dissolved } CO_2]}{\text{Gaseous } CO_2} \qquad \text{Where Gaseous } CO_2 = 10^{-3.5} \qquad \textbf{3.i}$$

$$K_0 = \frac{[H_2CO_3]^*}{pCO_2} \qquad [H_2CO_3]^* = [\text{Dissolved } CO_2] + [H_2CO_3] \qquad \textbf{3.ii}$$

$$K_1 = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} \qquad \textbf{3.iii}$$

$$K_2 = \frac{[H^+] \times [CO_3^{2-}]}{[HCO_3^{2-}]} \qquad \textbf{3.iv}$$

$$K_3 = \frac{[CaHCO_3^+]}{[Ca^{2+}] \times [HCO_3^-]} \qquad \textbf{3.v}$$

$$K_4 = \frac{[CaCO_3]}{[Ca^{2+}] \times [CO_3^{2-}]} \qquad \textbf{3.vi}$$

$$K_5 = \frac{[CaOH^+]}{[Ca^{2+}] \times [OH^-]} \qquad \textbf{3.vii}$$

$$K_{water} = [H^+] \times [OH^-] \qquad \textbf{3.viii}$$

$$K_7 = [Ca^{2+}] \times [CO_3^{2-}] \qquad \textbf{3.ix}$$

Each of these equilibria equations can be corrected for temperature change via an experimentally derived equation (See Appendix 1 and 2). These are the basic equations for any natural river system that has a pH above 5. The speciation equation that this model is based upon is similar to the Neal *et al.*, (1998) model where:-

$$\text{Predicted Alkalinity} = [HCO_3^-] + 2 \times [CO_3^{2-}] + [CaHCO_3^+] + 2 \times [CaCO_3] + [OH^-] \ [H^+] \qquad \textbf{3.x}$$

Comparing the alkalinity estimated in equation 3.3x with the measured alkalinity for the catchment requires an initial estimate of $EpCO_2$ this can be found again based on the Neal *et al.*, (1998) model the $EpCO_2$ for a natural stream is:-

$$EpCO_2 = \frac{\left(0.95\ Alkalinity\ + 10^{6-pH} + 10^{6+pH+LOG\left(k_{water}\right)}\right)10^{6-pH}}{\left(6.46\ - 0.0636T\right)\left(1 + 2.38\ 10^{pH+LOG\left(K_2\right)}\right)} \qquad \textbf{3.xi}$$

Values of $EpCO_2$ can be corrected for altitude again using the approach of:-

$$EpCO_2 = EpCO_{2\ calculated} \times \frac{\left(288\ - 0.0065\ altitude\ \right)}{288}^{5.256} \qquad \textbf{3.xii}$$

Once this corrected value of $EpCO_2$ has been calculated then the concentration of CO_2 in the water needs to be found. This can be done by using Henry's Law corrected for temperature (See Appendix 1; K_H, and equation 3.3.i). From this corrected value of Henry's Law a predicted concentration of CO_2 in the water, from the atmosphere, can be found by multiplying Henry's law constant corrected for temperature by the partial pressure of CO_2 in the atmosphere. Using flow data, in litres per second, from the field sites a flux value or a carbon export model can be estimated using the simple approach:-

$$Export = \left(mg/l\ Conc. \times Avg.\ Flow\ Rate\right) \times 86400 \times Number\ of\ days\ to\ next\ sample \qquad \textbf{3.xiii}$$

These values can simply be summed over a year and divided by the area of the catchment to give an export value in gC $m^{-2}y^{-1}$.

The above equations (Equations 3.i to 3.xiii) can be used to classify the species that dissolve and speciate in water with a pH above 4.5. This situation becomes more complex if the catchment has a pH below 4.5 because aluminium and DOC become important acidic species therefore the following equations including equations 3.i to 3.ix were used to determine the speciation reactions for the Hexhamshire Common field site Hex 1 blocked, Hex 2 unblocked, and Hex 3 blocked, and the Cowgreen blocked old field site.

Aluminium can speciate in the following ways:-

$$K_1 = \frac{\left[Al(OH)^{2+}\right]}{\left[Al^{3+}\right]\times\left[OH^-\right]} \qquad \textbf{3.xiv}$$

$$K_2 = \frac{\left[Al(OH)_2^{+}\right]}{\left[Al^{3+}\right]\times 2\left[OH^-\right]} \qquad \textbf{3.xv}$$

$$K_3 = \frac{\left[Al(OH)_3\right]}{\left[Al^{3+}\right]\times 3\left[OH^-\right]} \qquad \textbf{3.xvi}$$

$$K_4 = \frac{\left[Al(OH)_4\right]}{\left[Al^{3+}\right]\times 4\left[OH^-\right]} \qquad \textbf{3.xvii}$$

This now gives the major anions and cations that are important in this type of environment. The speciation equation for this equation can be determined in two different ways depending upon whether a charge balance equation is used or an acid base balance equation is used.

This reaction does not take into account the speciation of any organic components of the stream water. According to Dai *et al.*, (1996), organics will speciate via the following manner:-

$$K_{a1} = \left[Org^{3-}\right] \qquad \textbf{3.xviii}$$

$$K_{a2} = \frac{\left[Horg^{2-}\right]}{\left[Org^{3-}\right]\times\left[H^+\right]} \qquad \textbf{3.xix}$$

$$K_{a3} = \frac{[H_2 org^-]}{[Org^{3-}] \times [H^+]^2}$$

3.xx

Modifying the charge balance equation (Equation 3.xviii) to include these new species gives:-

$$\text{Electroneutrality Discrepancy} = 3 \times ([Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_4^-]) + 2 \times ([H_2CO_3^0] + [HCO_3^-] + [CO_3^{2-}]) + [HCO_3^-] + 2 \times [H_2CO_3^0] + [Al(OH)^{2+}] + 2 \times [Al(OH)_2^+] + 4 \times [Al(OH)_4^-] + 2 \times [Ca^{2+}] + [H^+] + [OH^-] + (3 \times [Org^{3+}] + 2 \times [HOrg^{2-}] + [H_2org^-])$$

3.xxi

The second way to speciate these different ions is via an acid-base reaction. This is the ability of an ion to either accept an OH^- ion or loose an H^+ ion. Depending on the number of ions it can either gain or loose depends on the multiplying number. For example based on Neal *et al* (1994):-

$$G_{acidity} = 2 * [H_2CO_3^0] + [HCO^{3-}] + 4 * [Al^{3+}] + 3 * [Al(OH)^{2+}] + 2 * [Al(OH)_2^+] + [Al(OH)_3^0] + [H^+] + [Horg^-] + 2 * [H_2org^0] - [OH^-]$$

3.xxii

However, this equation does not include the speciation of calcium. There were other species in the Neal *et al.,* (1998) equation but it was felt that these terms were insignificant in upland environments such as fluorine and ammonia. There were other species used that the author was unable to find temperature dependant stability constants for, such as the complexing of Aluminium with DOC as suggested by Neal *et al.,* (1998). It is also noted that the authors Neal and Dai use the same speciation model (ALCHEMI) and the charges on the organic ions is different, Dai references Schecher *et al.,* (1995)

paper whilst Neal references Schecher *et al.*, (1987) paper. It is assumed that the more modern paper by Schecher *et al.*, (1995) is correct and this will be incorporated into our speciation model:-

$$G_{acidity} = 2*[H_2CO_3] - 2*[CO_3^{2-}] + 4*[Al^{3+}] + 2*[Al(OH)^{2+}] - 2*[Al(OH)_3^0] - [Al(OH)^{4-}] + 2*[Ca^{2+}] - 2*[Ca(OH)_2^0] - 3*[Org^{3-}] - [Horg^{2-}] + [H_2org^-] - [OH^-] + [CaCO_3] + [H^+]$$

3.xxiii

Where there were no concentration values of dissolved aluminium, calcium, and DOC, a simple model was constructed where it was assumed that the total dissolved species was equivalent to the HCO_2^{-1} and CO_3^{2-} species. The iterative solving solution to find the total dissolved excess CO_2 concentration was then based on this value and the total alkalinity measurements. This excess CO_2 concentration where the total dissolved species is based on the HCO_3^{2-} and CO_3^{2-}, was also calculated for the results where concentrations of calcium, aluminium and DOC were measured. The two sets of results were regressed, and the regression equation used to correct the values where the total species in solution was based on the HCO_3^{1-} and CO_3^{2-} species, this lead to the following equation:

$$(R^2 = 0.994,\ n = 77,\ y = 1.026 \times EpCO_{2\ uncorrected} - 3.057)$$

3.4. Results

3.4.1. Determining dissolved CO_2 concentration

Determining the dissolved gaseous concentrations of CO_2 using the speciation model developed above (See section 3.3.5 and appendix 1) it was found that Hex 2 had the

highest concentration of dissolved CO_2 of up to 53.156 mg L^{-1}. The next highest concentration of dissolved CO_2 was from Hex 1 with a concentration of 38.674 mg L^{-1}. The field site with the lowest release was Hex 2 with an uptake of -0.486 mg L^{-1}. The site with the lowest average dissolved CO_2 concentration over the measurement period was Widdybank with an average concentration of 1.11 mg L^{-1}, and the grips with the highest average dissolved CO_2 concentration over the measurement period were Hex 1 and Hex 2 with respective average concentrations of 16.79 and 16.36 mg L^{-1}. These results can be shown by a graph of dissolved CO_2 concentration over time (Figure 3.2)

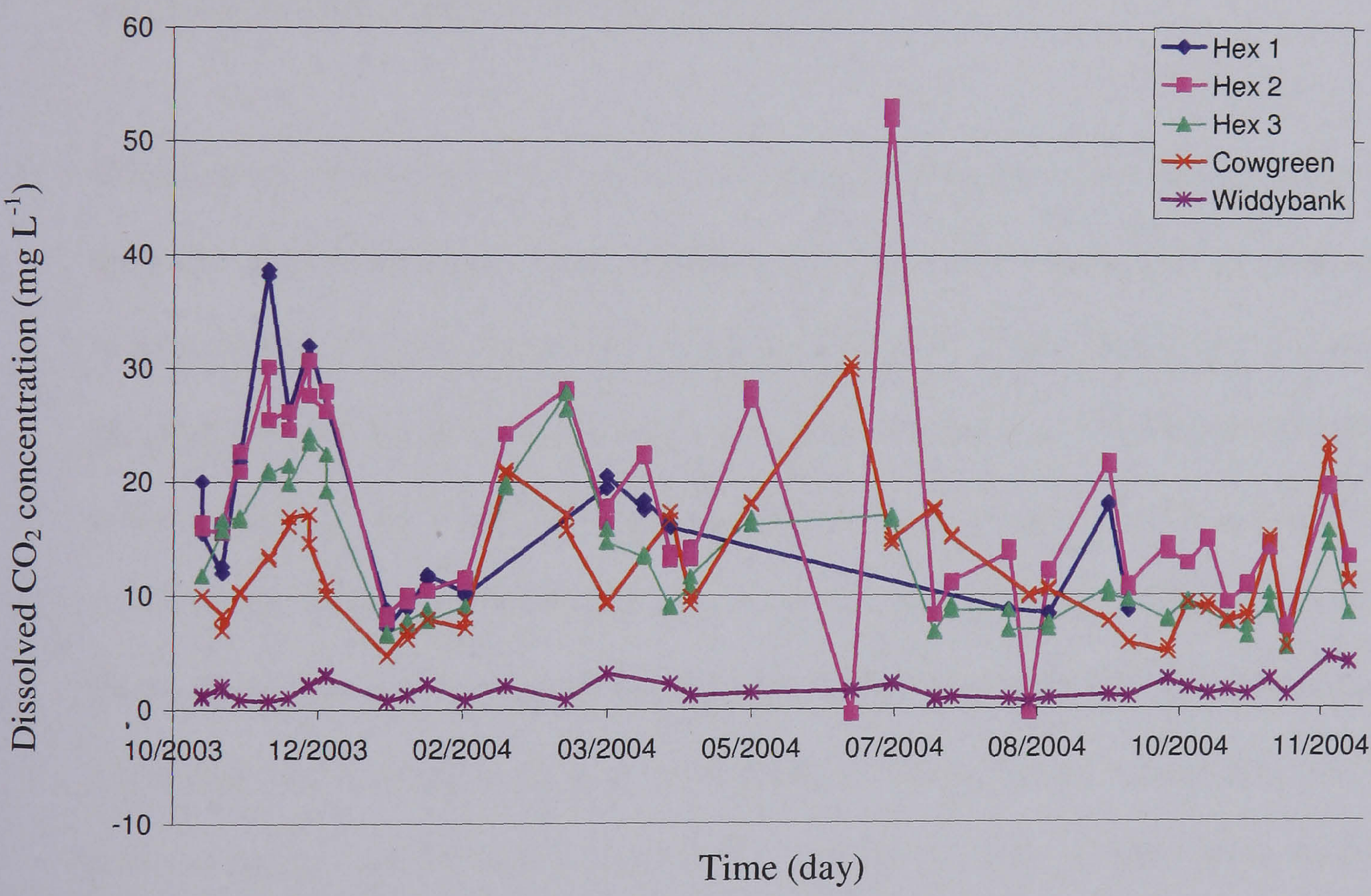

Figure 3.2 Dissolved CO_2 concentration over time

Hope *et al.*, (2004) reported values of dissolved CO_2 from a first order stream on upland peat of between 2.8 to 9.8 mg L^{-1}. The Hope *et al.*, (2004) site had a higher average

temperature (8^0C compared to 6.87^0C at Hexhamshire Common site) and the catchment area was larger (1.3 Km^2) than Hexhamshire Common (Hex 1 = $1800m^2$, Hex 2 = $7500m^2$, Hex3 = $2400m^2$) and Cowgreen catchments ($3500m^2$), and smaller than the Widdybank fell catchment area ($27500m^2$). This would have allowed for a greater proportion of the excess dissolved CO_2 to degas and evade the system before measurement from the Hope *et al.*, (2004) site and Widdybank. The pH at the Hope *et al.*, (2004) site (pH = 5.2) was also higher than the Hexhamshire Common (Hex 1 = 3.60, Hex 2= 3.24, Hex 3 = 4.05) and Cowgreen field sites (Cowgreen = 3.58), and lower than the Widdybank Fell field site (Widdybank = 7.47).

Worrall *et al.*, (2005), measured $EpCO_2$ values for two water treatment works on the Tees river and the Coquet river. These measurements taken much further down stream than measured here, however the measures of dissolved CO_2 in this project are in a similar geographical location in the North East of England. Worall *et al.*, (2005) reported $EpCO_2$ values of between 0.15 and 5.25 equating to dissolved CO_2 values of 0.04 and 1.85 mg C L^{-1} (between 0.147 and 19.25 $mgCO_2$ L^{-1}) at the Broken scar treatment works on the Tees. These values are comparable with the dissolved CO_2 measured here. The values at the Warkworth treatment works on the Croquet are slightly lower having dissolved CO_2 concentrations of 0.147 and 11 $mgCO_2$ L^{-1}. However, both of these water treatment works had a much higher pH compared to the gripped sites studied here, having pH values between 7.2 and, 9.75, which are comparable with the pH values from Widdybank. However Widdybank had much lower dissolved CO_2 values compared Worrall *et al.*, (2005) study.

When the concentration of dissolved CO_2 concentration is multiplied by the specific flow value at the time of sampling this gives the flux of CO_2 at the time of sampling. It was found that the greatest flux of carbon is from Widdybank with an export value of 121.88 mg L^{-1} s^{-1}. The site with the second carbon flux is Hex 2 with an export of 46.24 mg s^{-1}. The other three sample locations (Hex 1, Hex 3, and Cowgreen) have maximum flux values of 2.53 mg s^{-1}, 8.45 mg s^{-1}, and 13.11 mg s^{-1} respectively (See Figure 3.3).

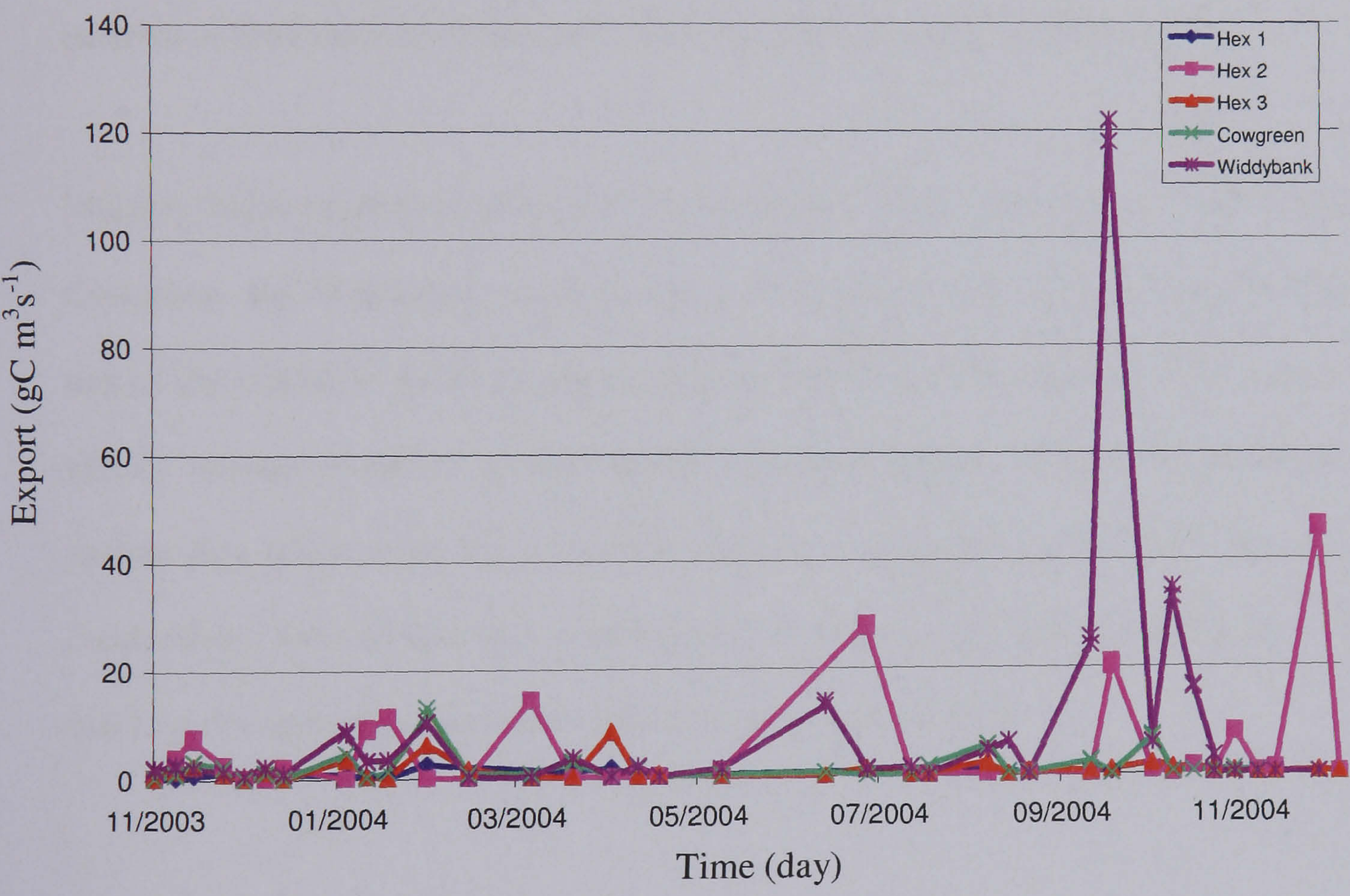

Figure 3.3 Carbon export over time

3.4.2. Determining the controls on dissolved CO_2 concentration

There are a number of potential controls or predictors that could affect or predict the amount of CO_2 released. They are; treatment or flow regime, season, rainfall, grip flow, conductivity and gaseous CO_2 flux. The simplest method for determining the significant controls or predictors on dissolved CO_2 is via statistical analysis of the results.

Multiple linear regression of the CO_2 concentration values from Hex 1, Hex 2, Hex 3, Cowgreen, and Widdybank, against; flow, conductivity, sum of daily rainfall (Sum in mm of the rainfall from the 15 minute data set for the day the dissolved CO_2 sample was taken), average of the 15 minute rainfall (Average amount, in mm, of rainfall on the sample day taken from the 15 minute data set), season, Log of flow, and Log of conductivity, showed that flow, conductivity, average of the daily rainfall Log of flow, and Log of conductivity were all significant, with an $R^2 = 40.7\%$.

Variable	P (n = 97)
Flow	0.050
Conductivity	0.001
Sum of daily rainfall	0.599
Average daily rainfall	0.007
Season	0.745
LOG flow	0.003
LOG conductivity	0.013

Table 3.1 Multiple Linear regression results for dissolved inorganic carbon

Where the regression equation is :-

$$Concentration = -18.6 - 0.392 \times Flow - 0.139 \times Conductivity + 1.45 \times Average\ daily\ rainf\ all - 1.51 \times Log\ Flow + 20.9 \times Log\ Conductivity \quad \textbf{3.xxiv}$$

These results (Table 3.1) show that dissolved CO_2 concentration in an upland peat system is linked to the conductivity of the grip, this means that the total amount of dissolved species within the grip system is a good indicator of the dissolved CO_2 within the system. From the regression equation (Equation 3xxiv) it can be seen that the relationship between conductivity and the concentration in solution is a negative relationship. Flow is also significant within the system, this means that there is a link between the amount of dissolved CO_2 within the system and the amount of water leaving the system, and is also a negative relationship with the concentration in the grip. As flow was significant in the statistical analysis it is therefore not surprising that rainfall is also significant.

The second statistical analysis performed on the data is multiple linear regression analysis again, but includes gaseous CO_2 flux in the analysis. The data from the Hexhamshire Common field site is the only data to be analysed in relation to gaseous CO_2 flux as this was the only site where gaseous CO_2 data was collected. The gaseous CO_2 data used was from the collars closest to grips Hex 2 and Hex 3, which corresponds to collars 1 and 2, and 7 and 8 (See Chapter 2, section 2.6.2 Field layout). Analysing the data using multiple linear regression where; flow, conductivity, sum of the daily rainfall, and rainfall daily average, net gaseous CO_2 flux, gross gaseous CO_2 flux, season, Log of flow, and Log of conductivity were all regressed against dissolved CO_2 concentration.

Variable	P (n = 53)
Flow	0.388
Conductivity	0.950
Sum of daily rainfall	0.888
Average of daily rainfall	0.957
Net gaseous CO_2 flux	0.442
Gross gaseous CO_2 flux	0.136
Season	0.043
LOG flow	0.640
LOG conductivity	0.404

Table 3.2 Multiple linear regression of Hexhamshire common data with net and gross gaseous CO_2 flux

As can be seen from Table 3.2, the only significant term is season (P = 0.043). The overall R^2 = 31.6%. These results suggest that there is no relationship between gaseous

CO_2 flux and dissolved CO_2 flux, and indeed including gaseous flux in the analysis makes other terms that were significant now insignificant.

To test whether treatment (Blocked, unblocked, blocked old, and natural) was statistically significant the data was analysed using ANCOVA taking the statistically significant terms greater than the 95% confidence level from the multiple linear regression analysis. These were; flow, conductivity, average rainfall, log flow and log conductivity (See Table 3.1), these were then used as covariates in the ANOVA analysis, and defining the different treatments, or grip types as the model gave the following results (Table 3.3).

Variable	P (n=97)
Flow	0.898
Conductivity	0.071
Daily Rainfall Average	0.019
Log Flow	0.190
Log Conductivity	0.033
Treatment	0.000

Table 3.3 ANCOVA on CO_2 concentration with treatment as model

As can be seen from Table 3.3 there is a significant difference between treatment types, showing that there is a difference in CO_2 concentration depending on grip type.

From the statistical analysis; flow, conductivity, daily average rainfall, log of flow and log of conductivity were all significant. Having found the significant variables which either affect or predict the concentration of dissolved CO_2 in solution, the next analysis is

to find the relation between each of these variables and dissolved CO_2 concentration. From the regression equation (Equation 3.xxv) it can be seen that the relationship between flow and dissolved CO_2 is a negative relationship suggesting that the lower the flow the greater the concentration of CO_2 in solution, and vice versa (Figure 3.4)

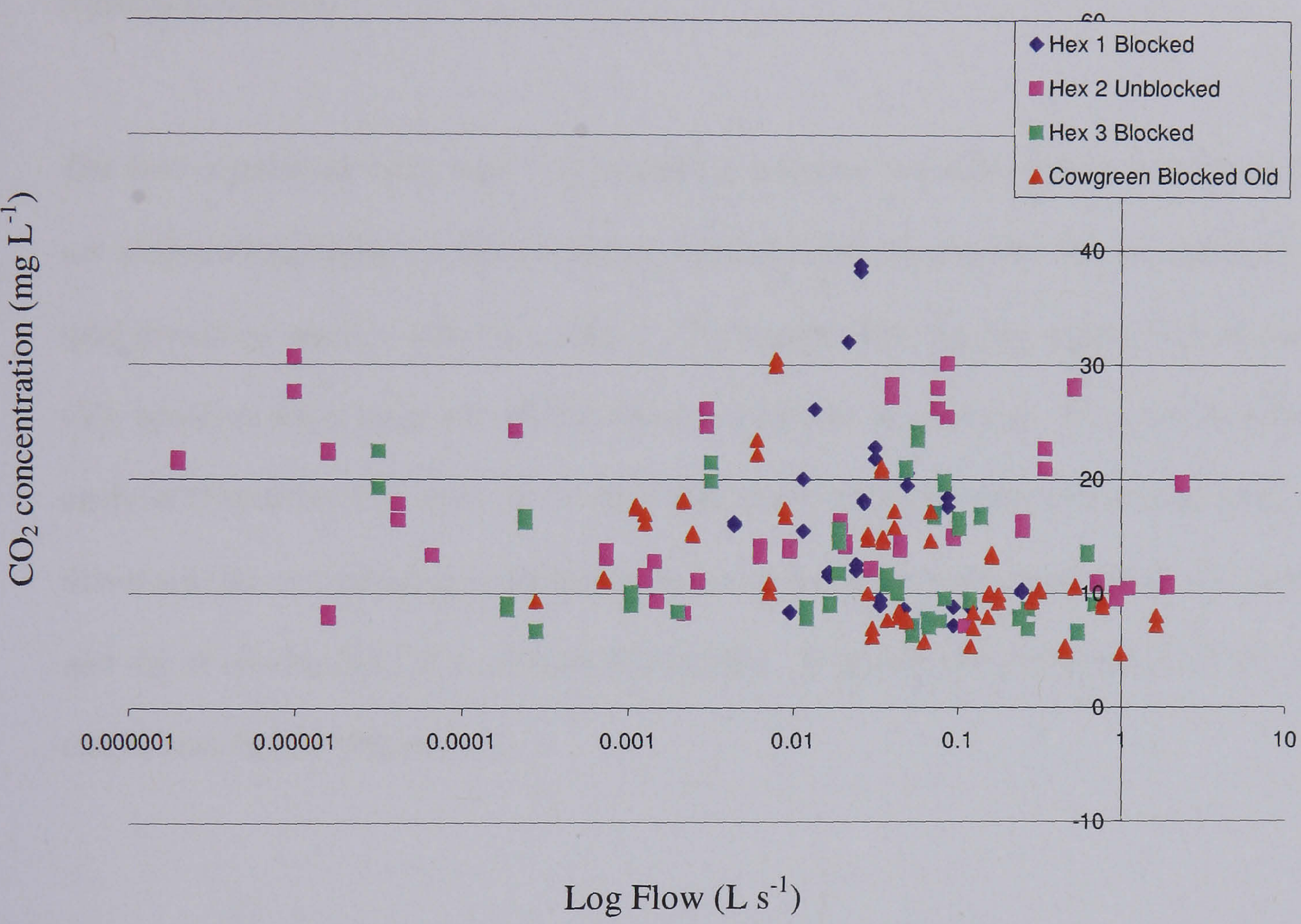

Figure 3.4 CO_2 concentration against Log of flow

As can be seen from the graph (Figure 3.4) there is a general trend for dissolved CO_2 concentration to be higher at lower flow levels, and have lower dissolved CO_2 concentrations at higher flows. From the graph it can also be seen that the concentration of dissolved CO_2 plateaus so that at higher flows the amount of CO_2 in solution does not dilute further. This is supported by the regression relationship between the dissolved CO_2 concentration and log flow. In this graph the flow data and dissolved CO_2 concentration

from Widdybank was not included as this site had much greater flow values compared to the other sites. Widdybank had a maximum flow of nearly 50 L s^{-1}, and a relatively low CO_2 concentration (See Figure 3.2), and the above relationship was masked and could not be seen visually, however the data from Widdybank was included in the multiple linear regression analysis.

The next significant term from the regression analysis is conductivity. Conductivity is not a controlling factor on the amount of dissolved CO_2 in solution, but a measure of the total dissolved species within a solution. The conductivity values suggest that dissolved CO_2 accounts for a large part of the dissolved species in solution. From the regression analysis (Equation 3.xxv) it can be seen that the relationship between conductivity and dissolved CO_2 is a negative relationship, however the relationship between dissolved CO_2 and log of conductivity is a positive relationship. A graphical representation of this data can be seen below (Figure 3.5)

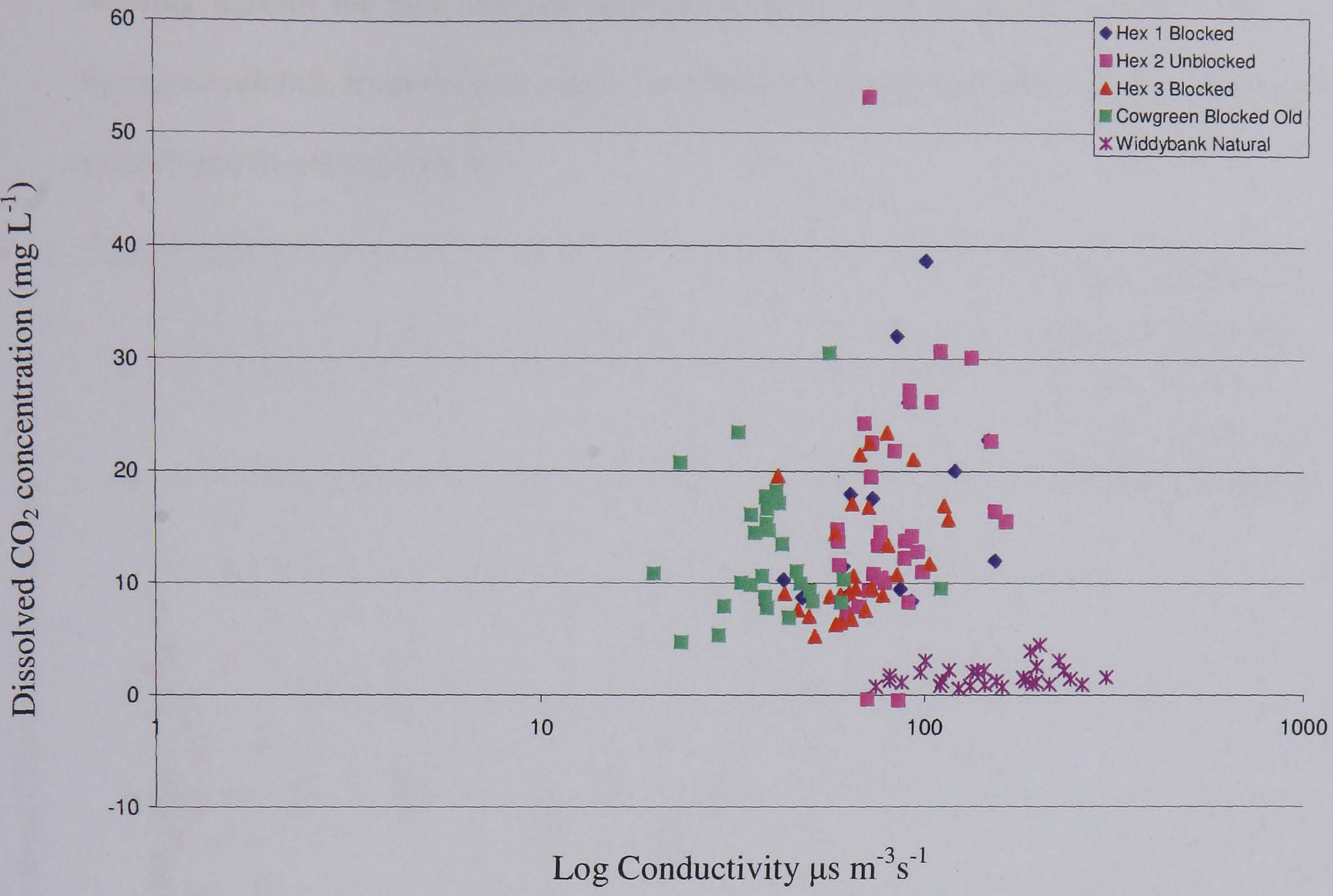

Figure 3.5 Dissolved CO_2 concentration against Log of conductivity

As can be seen from the graph (Figure 3.5) overall, there is a general positive relationship between conductivity and dissolved CO_2 concentration. From the graph it can also be seen that the four grips (Hex 1, Hex 2, Hex 3 and Cowgreen) all have comparable dissolved CO_2 concentrations, however Widdybank can be seen to have a much lower concentration compared to the four gripped locations.

As flow was significant it is not surprising that rainfall is also significant. From the regression analysis equation (Equation 3.xxv) the average daily rainfall has a positive relationship with dissolved CO_2. This is different from flow which had a negative relationship. This could mean that rainfall has, a flushing effect on dissolved CO_2,

flushing it from the peat into the drainage system, or is affecting a larger area, with increased rainfall, from the grip edge. Graphically the relationship between average daily rainfall and dissolved CO_2 is:-

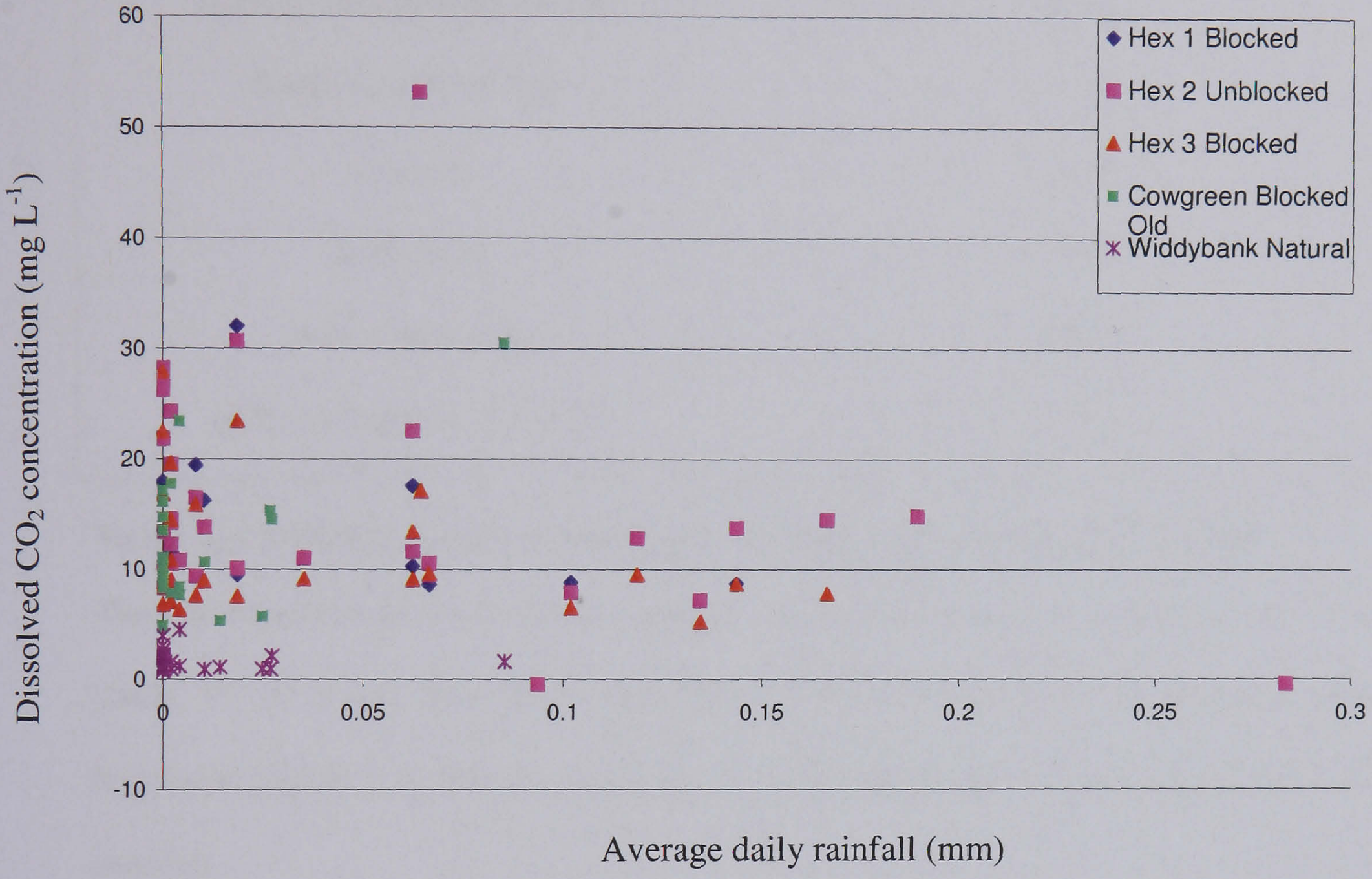

Figure 3.6 Average daily rainfall (mm) against dissolved CO_2 concentration

As can be seen from the graph (Figure 3.6) the relationship is a poor one, although statistically significant. It shows that when rainfall is higher there is generally a greater concentration of CO_2 in solution. From the above graph (Figure 3.6) it can be seen that there may be a log relationship between rainfall data and dissolved CO_2 concentration. A statistical analysis (Multiple linear regression) showed that there was no relationship between Log of average daily rainfall, and dissolved CO_2 (Table 3.4).

Variable	P (n=64)
Flow	0.093
Conductivity	0.007
Rainfall sum of daily rainfall	0.403
Rainfall daily average	0.050
Season	0.157
LOG Flow	0.039
LOG conductivity	0.035
LOG average daily rainfall	0.730

Table 3.4 Multiple linear regression with Log of average daily rainfall

The last treatment that affected the amount of dissolved CO_2 was the grip type. From Table 3.3 it can be seen that, with the significant terms from the multiple linear regression (Table 3.1) that the grip type is significant factor on the amount of CO_2 in solution.

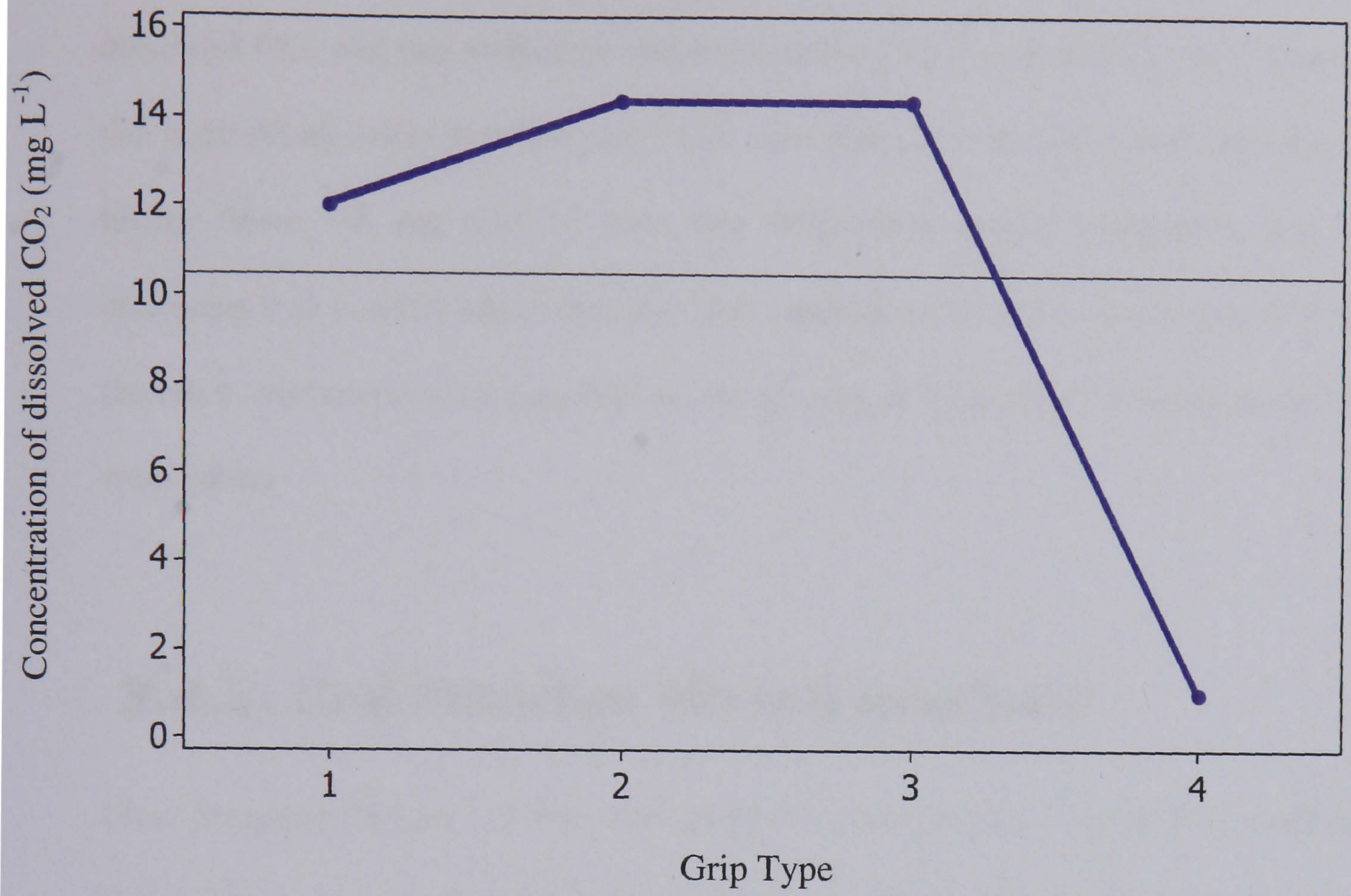

Figure 3.7 Main effects plot of dissolved CO_2 concentration against treatment, where 1 = Blocked (Hex 1 and Hex 3), 2 = Unblocked (Hex 2), 3 = Old blocked (Cowgreen), 4 = Natural (Widdybank)

A main effects plot is used when the mean response (Grip type) changes across the level of factors (Statistically significant terms from Table 3.1), and can therefore be used to compare the relative strength of the effects across factors. As can be seen from

Figure 3.7 the main difference between the different treatments is the difference between

the natural stream at Widdybank Fell and the blocked, unblocked and old blocked grips at

Hex 1, Hex 2, Hex 3 and Cowgreen. It can also be seen that the old blocked grip at

Cowgreen has a comparable dissolved CO_2 concentration to unblocked grip at

Hexhamshire Common.

It is noted that all of the analysis in this section suggest that the relationship between dissolved CO_2 and the predicting variables such as flow and rainfall, are all describing the same relationship between more soil pore water at low flows and more rainfall at higher flows. It can also be seen that Widdybank maybe misleading here as the catchment size is much larger than the other catchments and has a much greater flow than the other catchments, and may lead to out gassing of CO_2 before measurements of CO_2 were taken.

3.4.3. End Member Mixing Analysis

From the graph (Figure 3.5) the relationship between conductivity and CO_2 concentration looks like a 2 end member mixing diagram. From this graph (Figure 3.5) it is hypothesised that there are two end members, a ground water end member, which has a high conductivity, and low CO_2 concentration, represented by Widdybank, and a rainfall end member, represented by Cowgreen. There is a mixing of these two components representing rainfall flushing CO_2 from the aerobic peat. Calcium and aluminium should represent the soil pore water component, with high values at low flow, and low values at high flow.

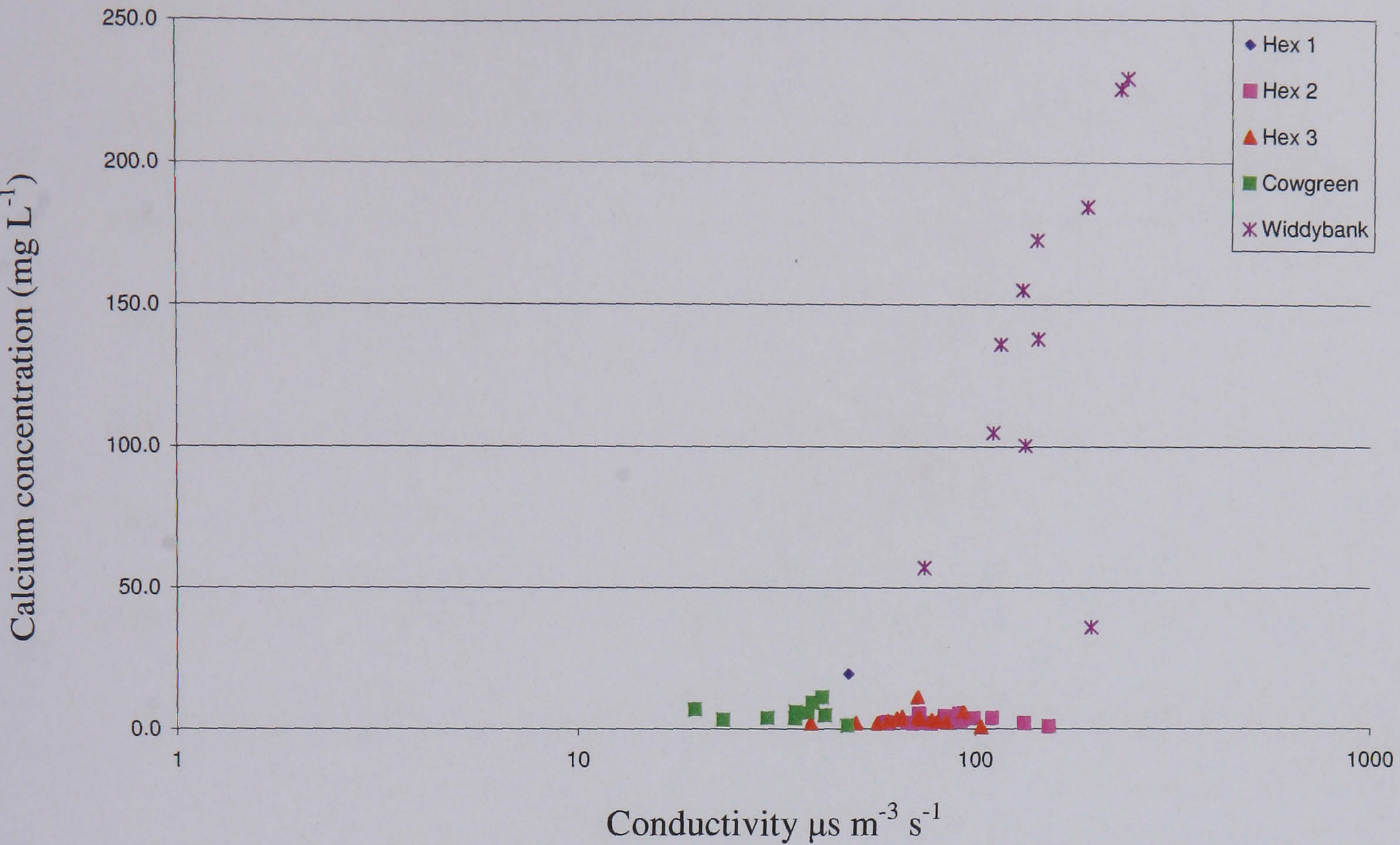

Figure 3.8 Calcium concentration against log of conductivity

As can be seen from the graph (Figure 3.8) this shows that Widdybank is a two end member system represented by high calcium at high conductivity representing contribution by ground water, and low calcium at low conductivities representing a rainfall component. It can also be seen that the Hexhamshire Common and Cowgreen system are different from the Widdybank system. As Widdybank may be a different system from the Hexhamshire Common system, a plot of aluminium against conductivity will exclude Widdybank as the pH was too high at Widdybank for aluminium to be in solution.

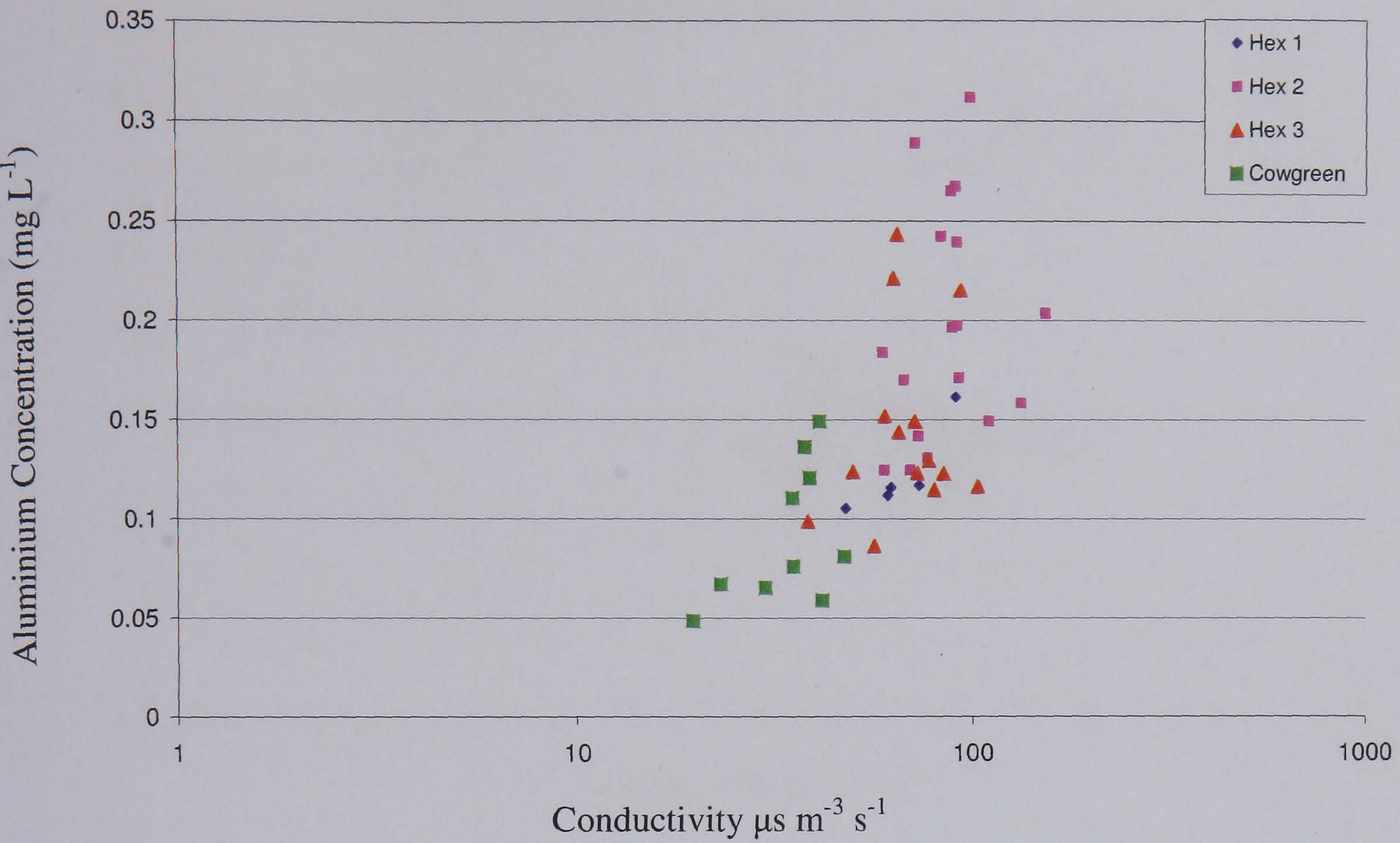

Figure 3.9 Aluminium concentration against log of conductivity

As can be seen from this graph (Figure 3.9), there again is a two component end member diagram, where aluminium is a proxy of the amount of flushing occurring within the system. In this graph, Widdybank data was removed as aluminium concentrations were below detection. A plot of pH against conductivity should show the relationship between the soil waters and rainfall with the different systems

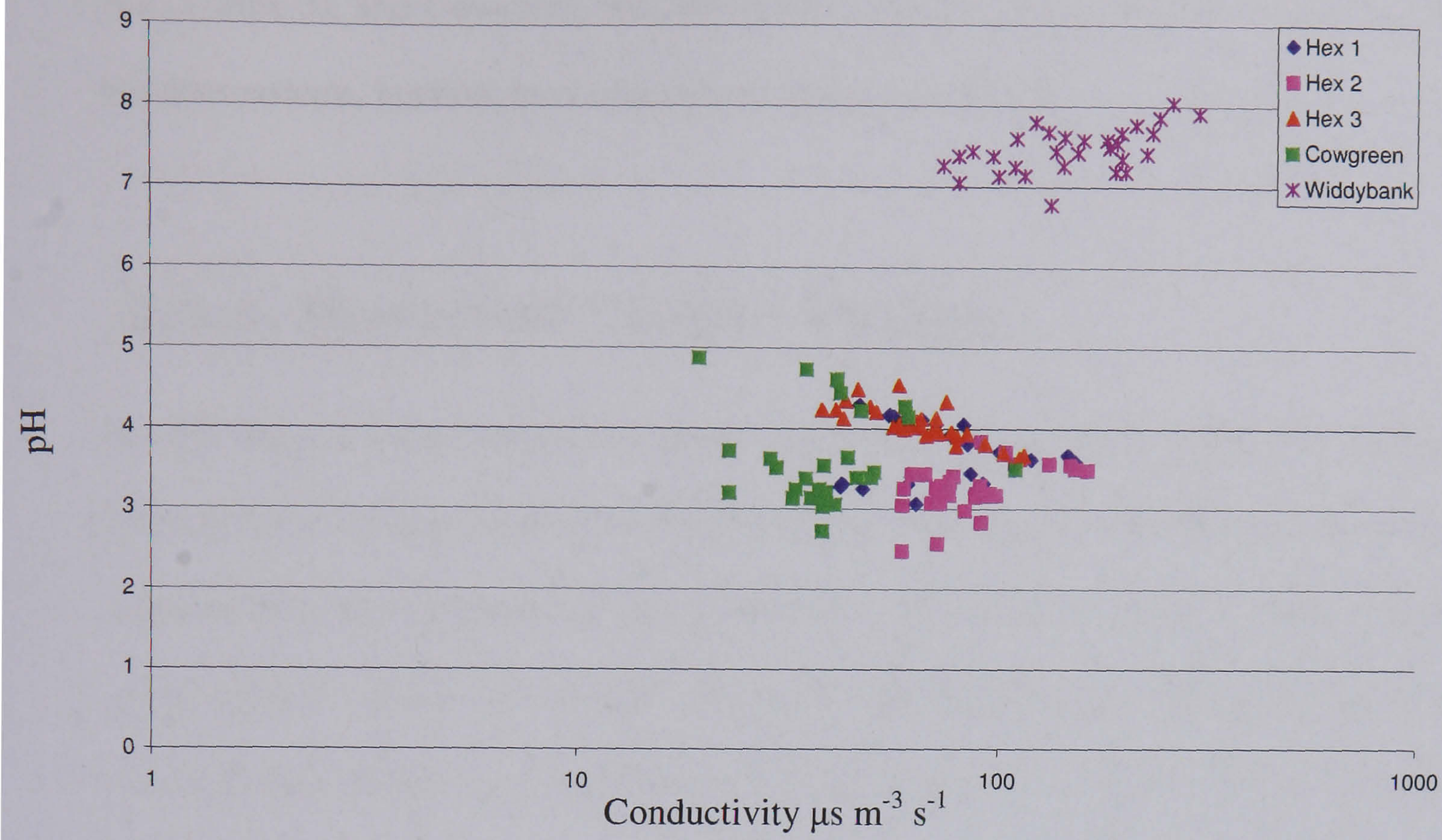

Figure 3.10 pH against log of conductivity

From this graph (Figure 3.10) it can be seen again that there the end member relationship breaks down into two separate systems. The first system is the grip system. In this system there is a relationship with pH and conductivity. The higher the pH the lower the conductivity, this would suggest that the system is becoming diluted by rainwater which is raising the pH, and during periods of lower pH the conductivity increased, suggesting a greater contribution from ground water sources. From the graph it can be seen that Widdybank has a much higher pH compared to the other sites and from the graph, the pH lowers when conductivity decreases. This could mean that the groundwater is enriched in calcium compared to the gripped sites, and thus having an alkaline pH overall, and that the rain water is diluting the calcium and as rain water is slightly acidic is lowering the pH at Widdybank.

Overall it can be said that there are two different systems, the gripped system (Hex 1,

Hex 2, Hex 3), and Cowgreen, and Widdybank. Both of these systems are a two end member systems, but both have different defining end members.

3.4.4. Dissolved Carbon Budget

In calculating a carbon budget for the different sites the speciation model was used to estimate the excess partial pressure of CO_2 in each water sample. Multiplying this by the measured flow and assuming the change between each reading is linear and each sample is representative of the excess partial pressure of CO_2 for the sample period the change in excess partial pressure can be plotted over time (Figure 3.3). As can be seen from the graph (Figure 3.3) there is no apparent seasonal pattern of dissolved CO_2 there are just large events when there appears to be a large amount of CO_2 fluxing into the drainage system. Calculating the carbon export for the site should show if there is any relationship to either the size of the catchment or the average flow from the catchment (Table 3.5)

Drainage system name	Carbon export (gC $m^{-2}y^{-1}$)	Drainage area (m^2)	Average Flow (l s^{-1})
Hex 1	10.556	1800	0.051
Hex 2	18.667	7500	0.270
Hex 3	16.667	2400	0.156
Cowgreen	14.286	3500	0.187
Widdybank Fell	5.881	27500	6.338

Table 3.5 Carbon export of dissolved CO_2

As can be seen from the table (Table 3.5) if the statement that: the larger the flow the greater the carbon export would be, is true then Widdybank Fell would be expect to have

the greatest carbon export values having the greater flow however as can be seen it has the lowest export values. The next greatest flow is from Hex 2, which has the greatest carbon export for all the sites. The site with the third greatest flow is the Cowgreen reservoir site, but has the forth lowest export values. From this table it can be said that the statement that the greater the flow the greater the carbon export is not true. From the table (Table 3.5) it has been assumed that all the sites are comparable with each other and are exporting the same concentration of carbon per unit area. If this assumption is false, as is more likely, then the only values which would be comparable are the export values from Hexhamshire common. At Hexhamshire Common the greater the flow the greater the amount of carbon exported. Another explanation could be that the greater the size of the catchment the greater time the dissolved CO_2 has to degas from the system. This statement is supported by the fact that Widdybank has been found to be a different system in end member mixing analysis, having a much high pH and conductivity than the other gripped systems.

The error in this method of calculating the carbon export was estimated from Worrall *et al.,* (2007 in press) who suggested that the largest source of error was the sampling rate. Worrall *et al.,* (2007 in press) degraded daily data to random monthly samples and found that the error to be 15.0%, and 8.9% when going from daily to weekly sampling. The approach used in the estimation of the budget has an inherent error of 3.3% (Harriman et al., 1998) giving an error in the excess dissolved CO_2 budget of 12.2%. This would leave the error for this study to be between the two values as the samples were collected weekly during winter and spring, and every three weeks during the summer. Nine months had

samples collected weekly and 3 months had samples collected every three weeks. Assuming error is scaled pro rata to the sampling rate then the cumulative error of 12.9% over the year. From each of the five sample sites (Hex 1, Hex 2, Hex 3, Cowgreen, and Widdybank) there were 36 samples taken over the year (Unless there was no sample to be taken due to freezing or drying out). Including this error in the carbon budgets from Table 3.5 shows the maximum and minimum carbon exports from each site.

Drainage system name	Carbon Export (gC $m^{-2}y^{-1}$)	Maximum export (=export + 12.9%)	Minimum Export (=export – 12.9%)
Hex 1	10.556	11.92	9.19
Hex 2	18.667	21.06	16.26
Hex 3	16.667	18.82	14.52
Cowgreen	14.286	16.13	12.44
Widdybank	5.881	6.64	5.12

Table 3.6 Carbon export including errors

Taking the gross CO_2 fluxes calculated in chapter 2, section 2.4.5.3, table 2.10 (Predicted net and gross CO_2 flux based upon experimentally defined GP_{max}), and comparing them to the total fluxes of dissolved CO_2 shows that the greatest release of CO_2 is via gaseous fluxes of CO_2 rather than dissolved CO_2. However, dissolved CO_2 fluxes are unaffected by PAR levels, and will, at no time during the cycle, take up CO_2 as the plants on the peat surface will. The net gaseous carbon balance (where net flux = primary productivity flux + gross flux) for the collars closest to Hex 2 grip is -13.36 gC $m^{-2}a^{-1}$ when this is compared to dissolved gaseous carbon export of 18.667gC $m^{-2}a^{-1}$ for the Hex 2 grip, it

can be seen that the peat is taking up gaseous carbon and releasing dissolved CO_2. However, the carbon export from the net collar bordering Hex 3 is 56.855 gC $m^{-2}a^{-1}$, when compared to 16.667 gC $m^{-2}a^{-1}$ for the dissolved carbon export for Hex 3 shows that for these gaseous collars they have a larger carbon export than dissolved carbon export. The export of dissolved CO_2 can be seen from Table 3.5, which shows that the net gaseous fluxes have a greater range of CO_2 flux, with one collar taking up CO_2 and the other releasing CO_2.

The average gaseous carbon release for the Hexhamshire Common site is 17.73 gC $m^{-2}a^{-1}$, compared to the average dissolved CO_2 export of 17.667 gC m^{-2} a^{-1} for Hex 2 and Hex 3 shows that the two export figures are very similar. When the dissolved and gaseous figures are combined and scaled up for the area of Hex 2 (7500m^2), and Hex 3 (2400m^2) shows that the area lost in the sample year an average of 0.3504 tonnes C for the whole year making this field site a small source of CO_2.

3.4.5. Geology or peat based sources of CO_2?

To find whether the source of dissolved CO_2 in the drainage system is from either the peat or weathering of the underlying geology, the chemistry of the water can be used. If the underlying carbonate strata has been weathered to produce an excess of CO_3^{2-} in solution there will be a corresponding increase in the amount of Ca^{2+} ion. Therefore looking at the average calcium concentrations in solution will give some measure of the source.

Grip/Stream name	Average calcium concentration (mg L^{-1})
Hex 1 - Blocked	4.9
Hex 2 - Unblocked	2.9
Hex 3 - Blocked	3.4
Cowgreen - Blocked Old	5.4
Widdybank - Natural	128.1

Table 3.7 Average calcium concentrations for each sampling site

As can be seen from Table 3.7 Widdybank Fell clearly has the greatest concentration of calcium, much greater than the calcium concentration in any of the other drainage system. Therefore, the source of dissolved CO_2 at Widdybank Fell comes mostly from weathering of the underlying geology. Widdybank Fell has a much higher pH than the other four sample site, having an average pH of 7.5, whilst the other sample site have pH's ranging from 3.24 to 4.05. The most likely scenario is a neutralisation reaction is occurring. From this it can be concluded that there is a contribution to the Widdybank Fell hydrological system of calcium carbonate which is neutralising the acid content of the solution and increasing the calcium concentration, and the Hexhamshire Common site and the Cowgreen site have a carbonate neutral substrate, that is, an underlying geology that is not carbonate based.

End member analysis of calcium concentration with respect to flow shows that calcium concentration at Hexhamshire Common and Cowgreen fields sites is comparable and produces a hyperbola curved graph (Figure 3.11)

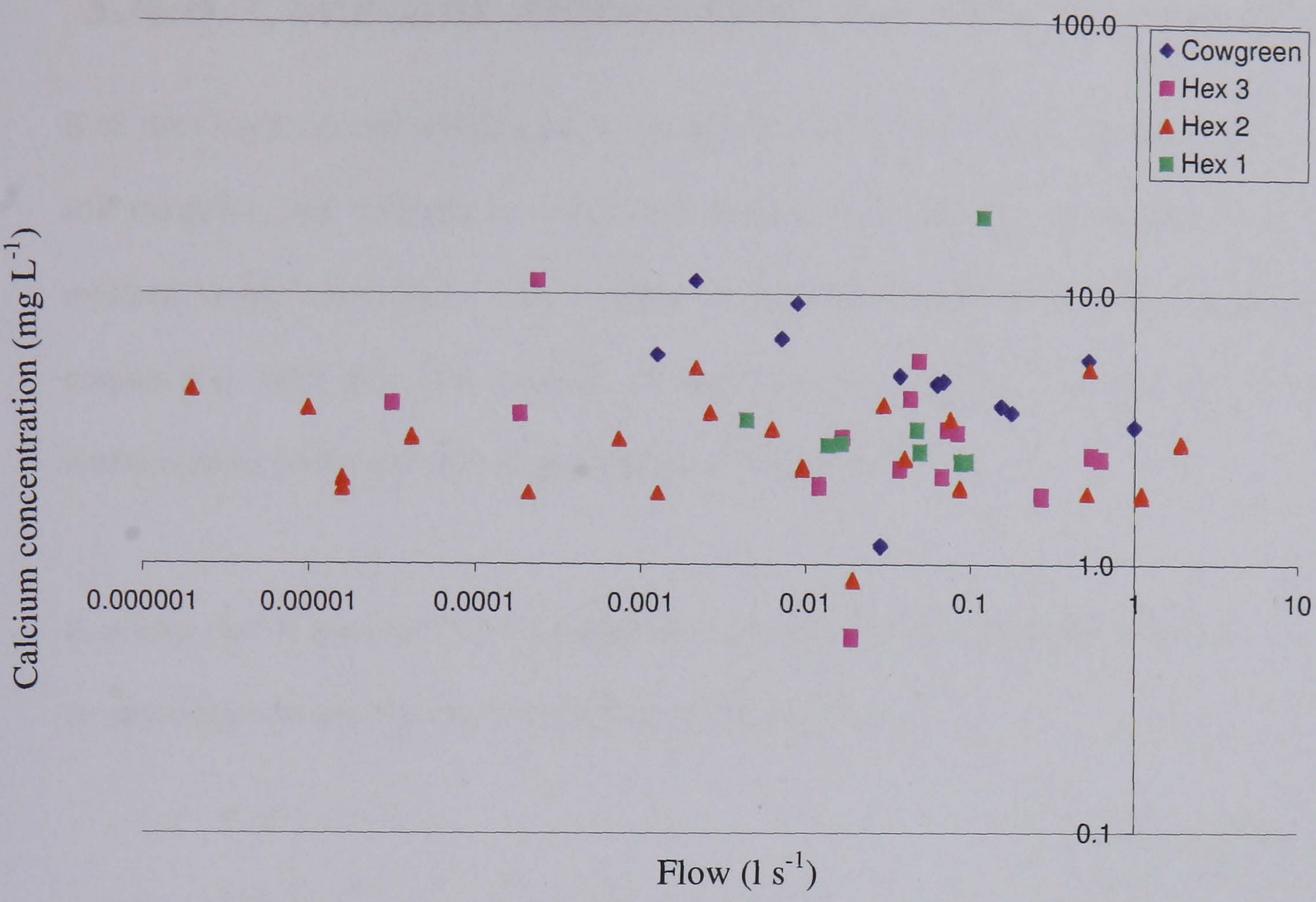

Figure 3.11 End member analysis of calcium concentration with respect to flow

From the graph (Figure 3.11) it can be seen that a low flow the maximum calcium concentration is 19.3 mg L^{-1}, from Hex 1. A reason for Hex 1 having the greatest concentration of calcium, is because Hex 1 ran dry over the summer, whilst the increased temperature would have increased the weathering of any carbonate material in the peat, and a rainfall event would flush the weathered calcium into the grip system. The calcium data from Widdybank was not included in this graph (Figure 3.11) because Widdybank had a much greater flow and calcium concentration compared to the other grips, and masked the relationship shown above, and has already been shown to be incomparable with the other results from the gripped systems.

3.4.6. Constant mechanism for CO_2 produced?

If all the CO_2 produced within peat is produced by the same mechanism i.e. respiration of soil microbes, and different environmental factors determine by which pathway CO_2 is released to the atmosphere. By looking at the total dissolved CO_2 flux produced in conjunction with the total amount of gaseous CO_2 released, should give a better understanding of the overall carbon budget of upland peat.

A scatter plot of gaseous CO_2 flux against dissolved CO_2 flux, should show the relationship between the two carbon fluxes (Figure 3.12).

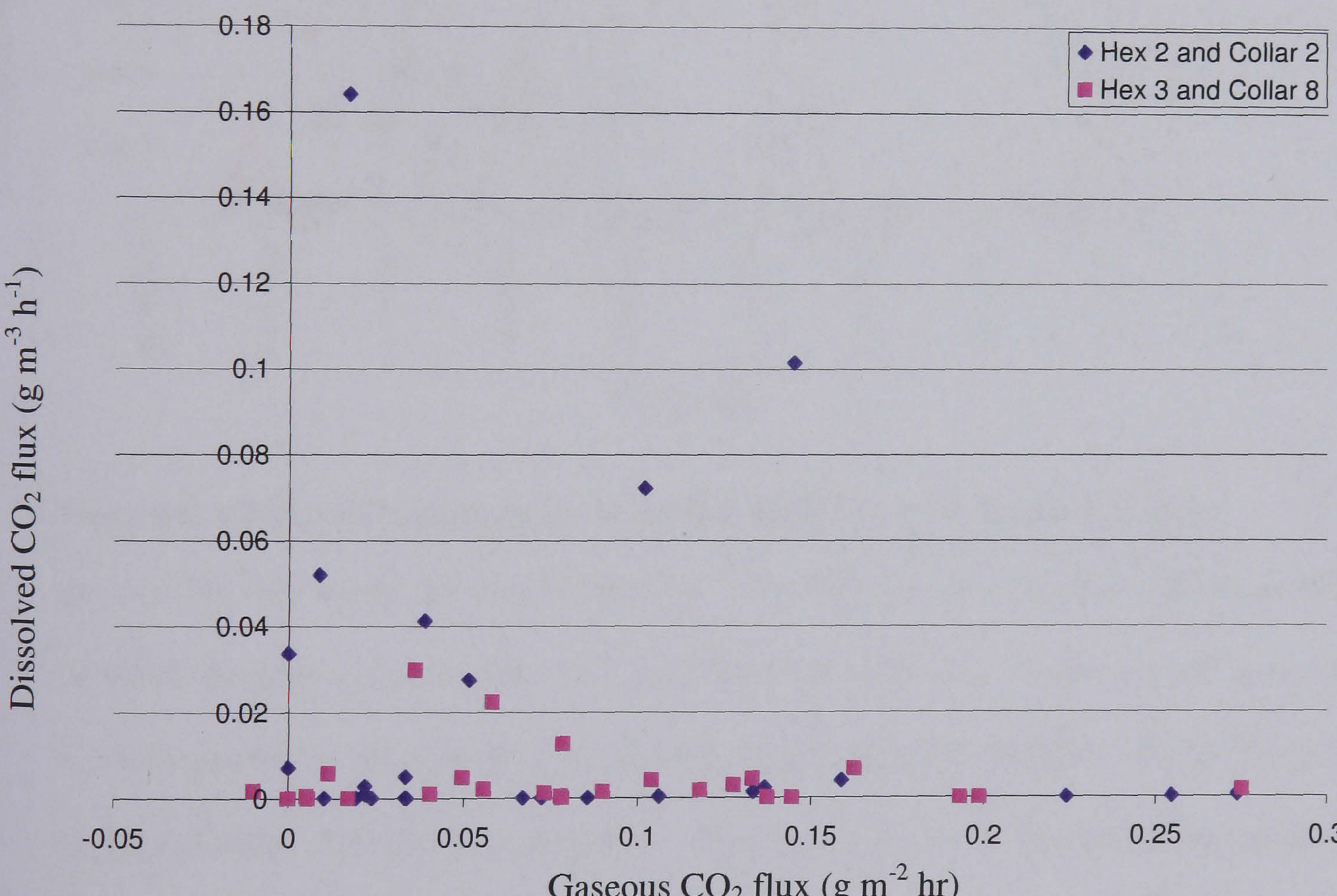

Figure 3.12 Gaseous CO_2 flux against dissolved CO_2 flux

As can be seen from this graph (Figure 3.12) there is no direct relationship between the

two carbon fluxes. This is supported by the statistical analysis of the two fluxes which showed that at the 95% confidence level the data was insignificant (P= 0.450, R^2= 1.1, n=55). This leaves a visual comparison between gaseous flux and dissolved flux over time.

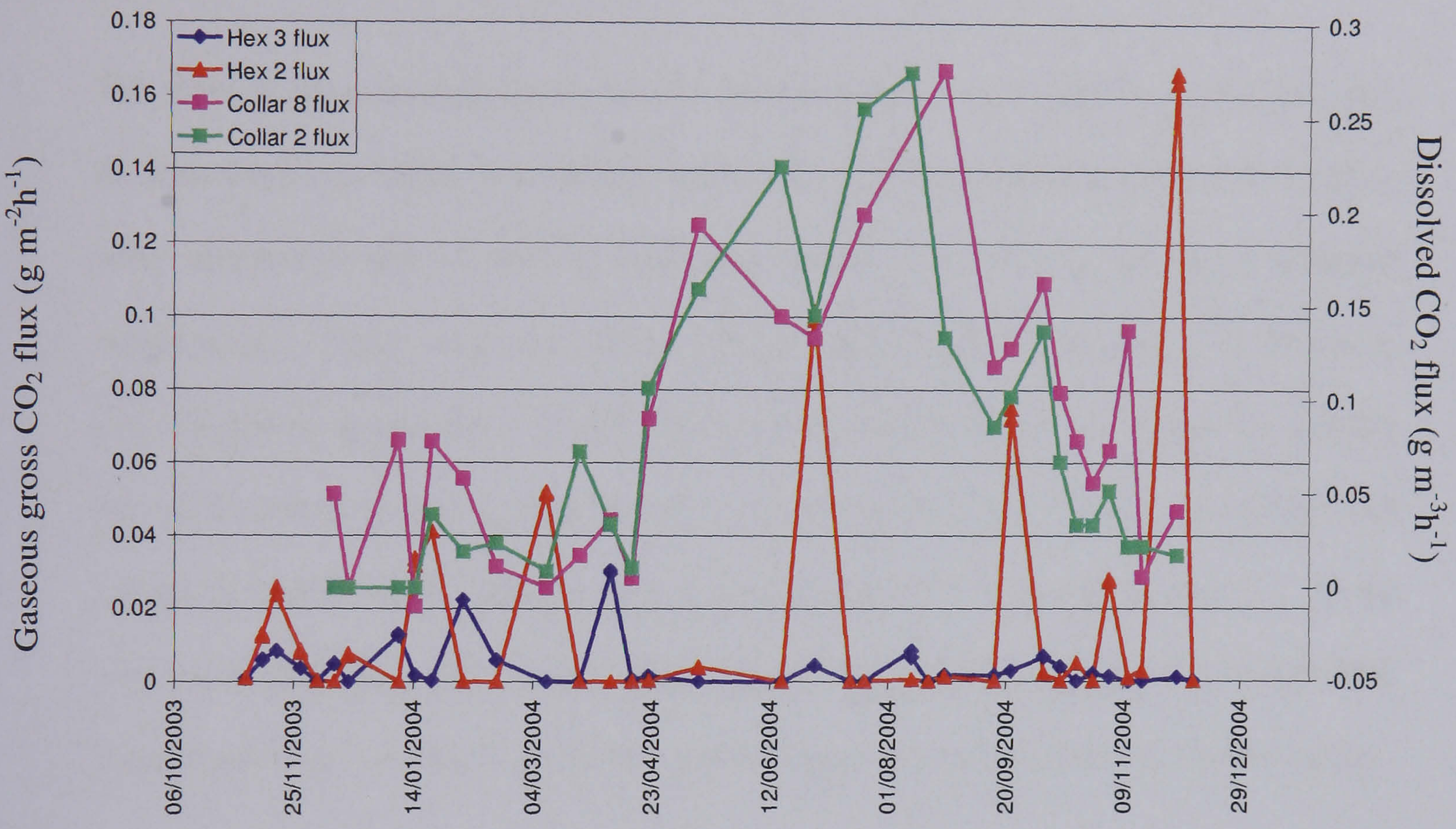

Figure 3.13 Visual comparison between gaseous and dissolved flux

As can be seen from the graph (Figure 3.13) there is no immediate visual relation between the gross gaseous CO_2 flux and dissolved CO_2 flux. There is, however, one event happening in the middle of the sample period, on the 01/07/2004, which cannot be explained either visually or statistically. This was a series of rainfall events after the previous gaseous flux measurement. The average rainfall for the measurement period (~1 year) was 3.69mm d^{-1} whilst the average for this wet event was 4.96mm d^{-1}, and the

average daily rainfall for the time between the two previous gaseous flux readings was 1.19mm d^{-1}. This event shows that there was a large decrease in the gross gaseous fluxes and a corresponding increase in the dissolved CO_2 flux. There were, however, other larger fluxes of dissolved CO_2 with no corresponding decreases in gaseous CO_2 flux.

The gross gaseous measurements of CO_2 from chapter 2 were used in conjunction with the dissolved CO_2 fluxes from Hex 2 and Hex 3. The dissolved and gaseous CO_2 fluxes were summed to give, hopefully, the total respiration values for the site at different temperatures. There were four collars used to measure gross CO_2 flux, 2, 4, 6, and 8, (See chapter 2, section 2.3.1 for full details of the field layout and experimental design), the collar closest to Hex 2, namely collar 2 were summed with the dissolved CO_2, and collars 6, and 8 were summed with the dissolved CO_2 fluxes from Hex 3. In the regression analysis collar 4 was excluded as it could not be said whether the dissolved fluxes from Hex 2 or Hex 3 would be contributing to the overall CO_2 flux for that collar.

Using multiple linear regression to analyse the summed flux values with respect to water table depth and soil temperature. It was found that soil temperature was significant (P = 0.000, n = 57), with the overall $R^2 = 68.6\%$. This regression showed that soil temperature was still significant (P = 0.000, n = 57), whilst compared with the overall $R^2 = 68.9\%$, for just the gross fluxes, showing that there is no improvement in the amount of variance explained by summing dissolved and gaseous CO_2 flux.

A second approach is to remodel the Lloyd and Taylor equation (Lloyd et al., 1994) with

respect to R_{10} values. From Chapter 2 section 2.4.5.1 equation 2.v, R_{10} is defined as a constant respiration rate at 10^0C. There were several different possibilities of improving the R_{10} values for each collar. Each gross flux collar was summed with the corresponding dissolved flux either from Hex 2 or Hex 3. Whether the gross flux was summed with the dissolved CO_2 fluxes from Hex 2 or Hex 3 depends on the position of the water table with respect to the other water table depths. This lead to the assumptions that Collar 2 would be summed with the dissolved from Hex 2 as Collar 2 had the deepest average water table, whilst the next collar across the transect, Collar 4, had the shallowest water table depth, therefore the below ground water must have flowed from collar 4 towards collar 2 and into Hex 2. The same can be said of collars 6 and 8, both having deeper water table depth than collar 4, so below ground water must have run from collar 4 passed collars 6 and 8 and into Hex 3. This left collar 4, and whether the dissolved CO_2 fluxes from Hex 2 or Hex 3 should be summed with the gross fluxes from collar 4. This was solved by simply summing collar 4 fluxes with hex 2 and regressing against the predicted Lloyd and Taylor fluxes then summing the collar 4 fluxes with the fluxes from hex 3 and performing the same regression. The regression with the highest R^2 value was thought to have the greatest contribution to the total respiration value for collar 4, and therefore defined the below ground water movement. Summing the dissolved and gaseous CO_2 fluxes and reiterating the Lloyd and Taylor equation to resolve R_{10} for each of the gross collars gave the following results. A simple graph of all the gross fluxes from all the collars plotted against the best fit Lloyd and Taylor model from chapter 2, section 2.4.5.1 shows the relationship between the fluxes.

Summing the dissolved and gaseous CO_2 fluxes led to some problems, as there were some sample days when either a gaseous sample or dissolved gas sample was not measured. All these results were excluded from the comparison (Figure 3.14).

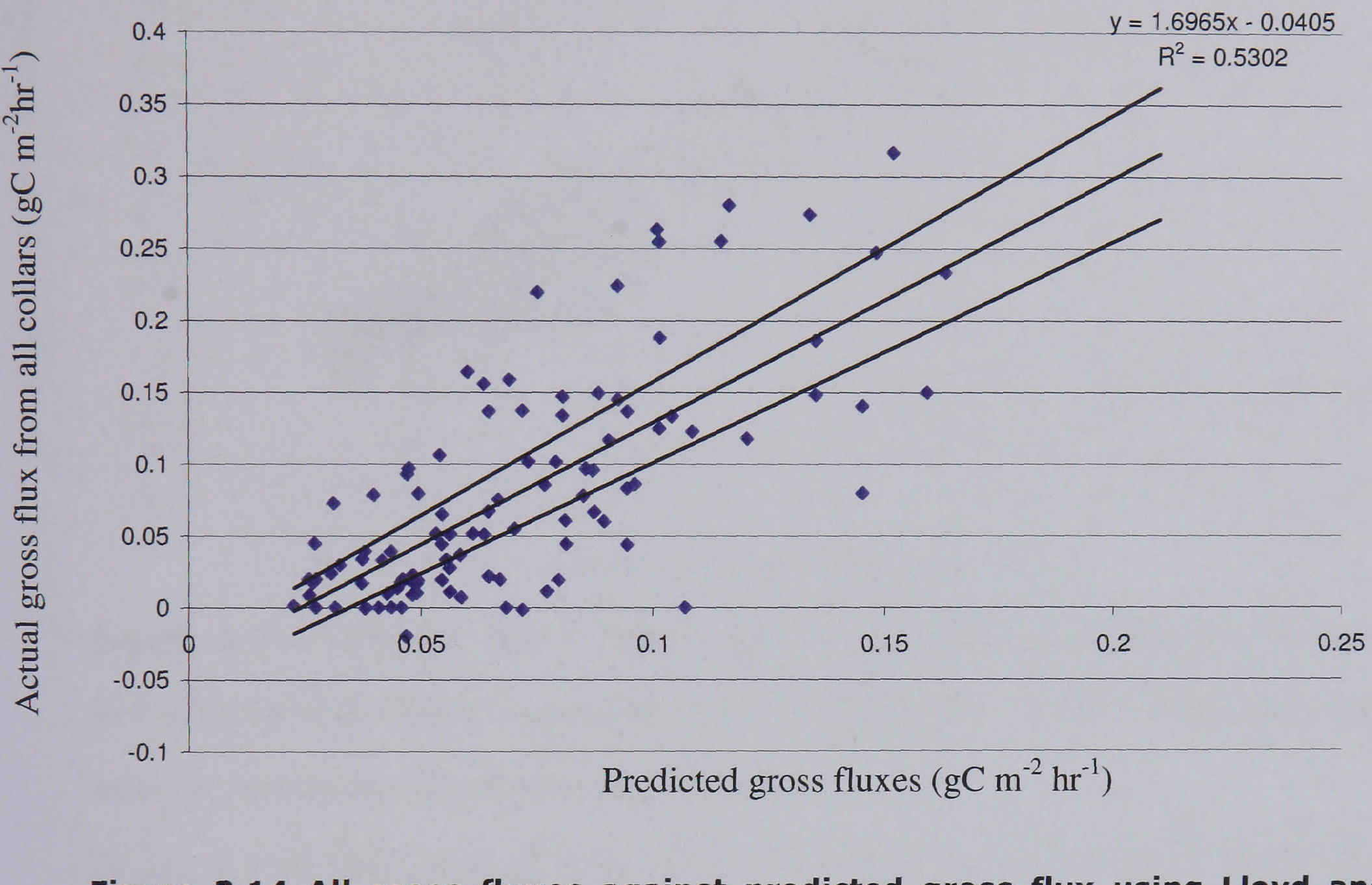

Figure 3.14 All gross fluxes against predicted gross flux using Lloyd and Taylor excluding gross flux data where there was not both gaseous and dissolved measures of CO_2. Also, best fit minimum and maximum error lines

Summing the dissolved fluxes and gross gaseous fluxes as discussed above, predicting revised R_{10} values for each collar and predicting the gross flux using Lloyd and Taylor, and assuming that Hex 2 contributed to the total flux from collar 4 gave the following graph (Figure 3.15)

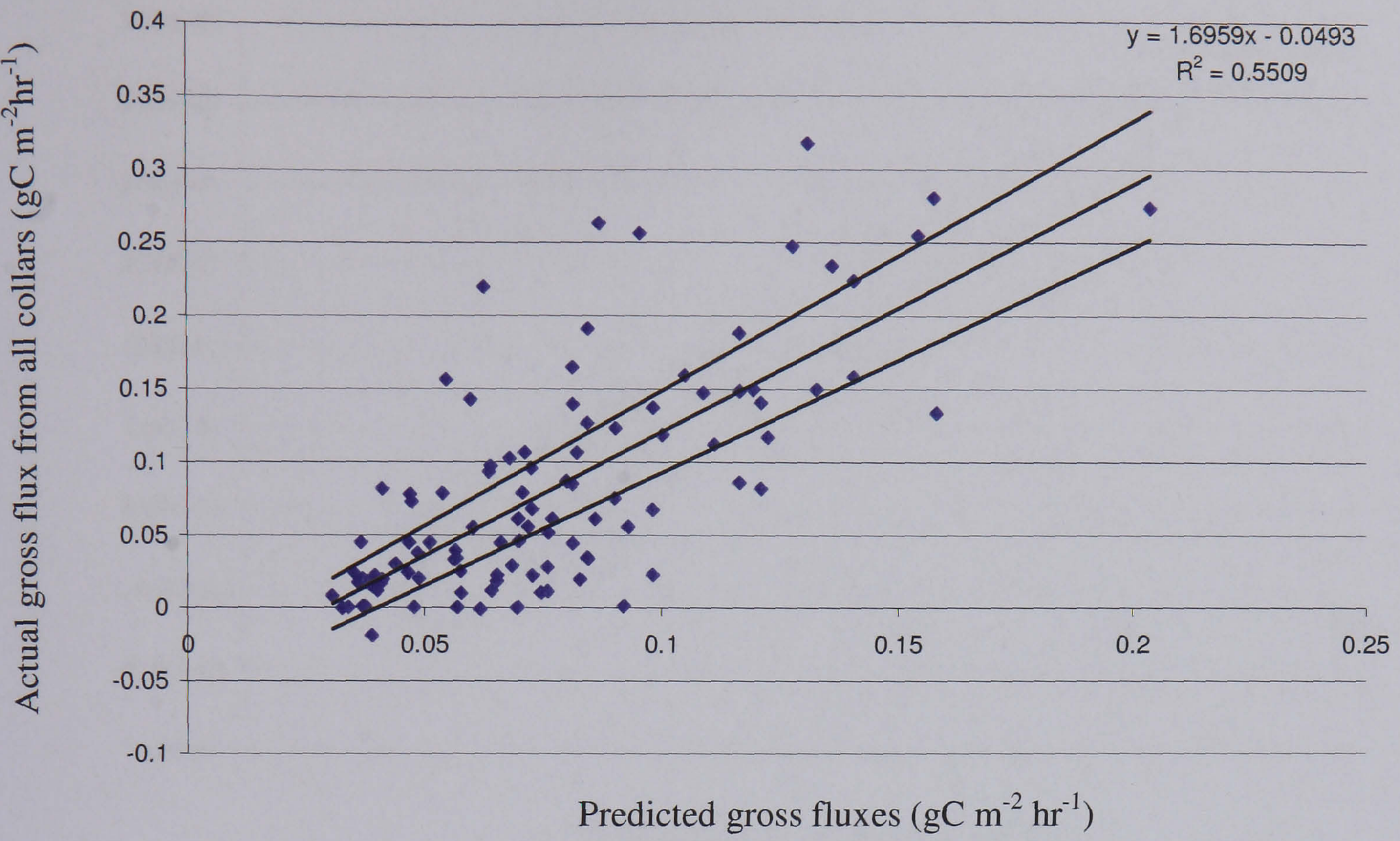

Figure 3.15 Gross CO_2 flux + dissolved CO_2 flux against predicted gross flux using Lloyd and Taylor assuming Hex 2 contribute to collar 4 total flux with best fit maximum and minimum error lines

As can be seen from the graph (Figure 3.15) the relationship has improved over the best fit estimates from just gross gaseous flux. That last graph is similar to Figure 3.15, but this time assumes that Hex 3 flux contributes to the overall flux of collar 4.

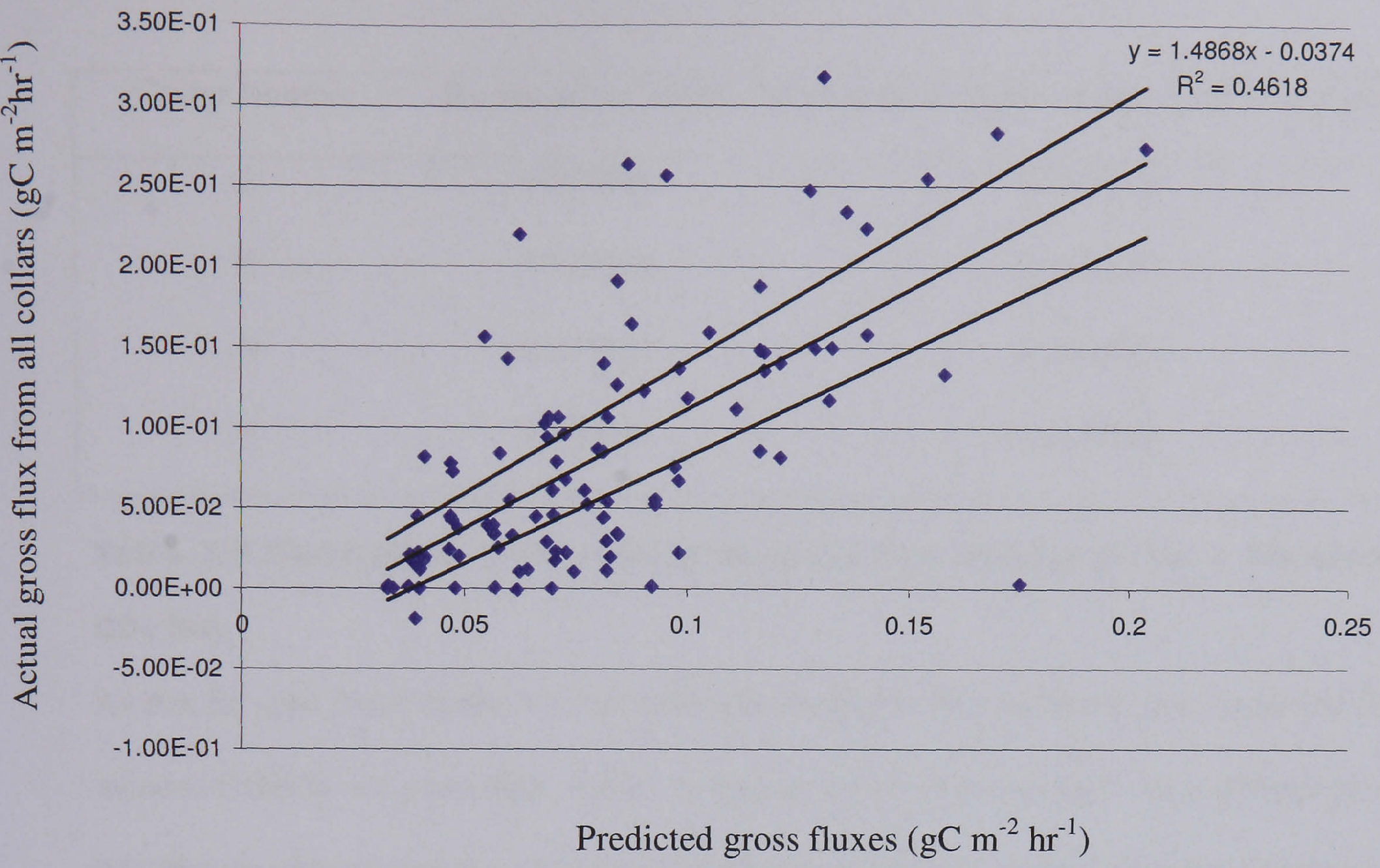

Figure 3.16 Gross CO_2 flux + dissolved CO_2 flux against predicted gross flux using Lloyd and Taylor assuming Hex 3 contribute to collar 4 total flux with best fit, maximum minimum error lines

As can be seen from the graph (Figure 3.16) the relationship is a poorer one than assuming that Hex 2 contributes to the total flux for collar 4. Therefore, it can be said that the deepest water table depth lies between collar 4 and 6. Overall there has been an improvement to the fit of the Lloyd and Taylor model to the measured fluxes, however how has this affect the R_{10} values for each collar?

Collar Number	R_{10} for gross fluxes	R_{10} for gross fluxes + dissolved CO_2 fluxes
2	0.087001	0.132152
4	0.075734	0.102339
6	0.127131	0.109483
8	0.136517	0.1137196

Table 3.8 Comparison of R_{10} values for gross flux and gross flux + dissolved CO_2 flux

As can be seen from Table 3.8 the difference between the maximum and minimum R_{10} value is 0.04952 for gross flux, whilst the gaseous and dissolved flux has a difference of 0.02981 suggesting that the values are trending towards a common R_{10} value, suggesting that as more variables are explained these values may become the same. From the table (Table 3.8), it can be seen that the sum of the R_{10} values have increased for dissolved gases and gaseous gases compared to the gaseous gasses, this is to be expected as both carbon fluxes were positive and summed. The main difference between the R_{10} values for the gaseous and the gaseous and dissolved fluxes is for collar 2 where the R_{10} value increased from 0.087001 to 0.132152. This increase in R_{10} value could be explained by the increase of loss of CO_2 into the drainage system due to ground water flow. This could mean that there is a relationship between water table depth and the amount of CO_2 produced from the single mechanism of CO_2 production. The steep gradient between collar 2 and collar 4, means, proportionally more CO_2 was dissolved into the drainage system than released as a gas when compared to the shallower gradient between collars 6 and 8 and 2. Therefore a plot of the redefined R_{10} values against average water table

depth for each gross collar will reveal any relationship (Figure 3.17).

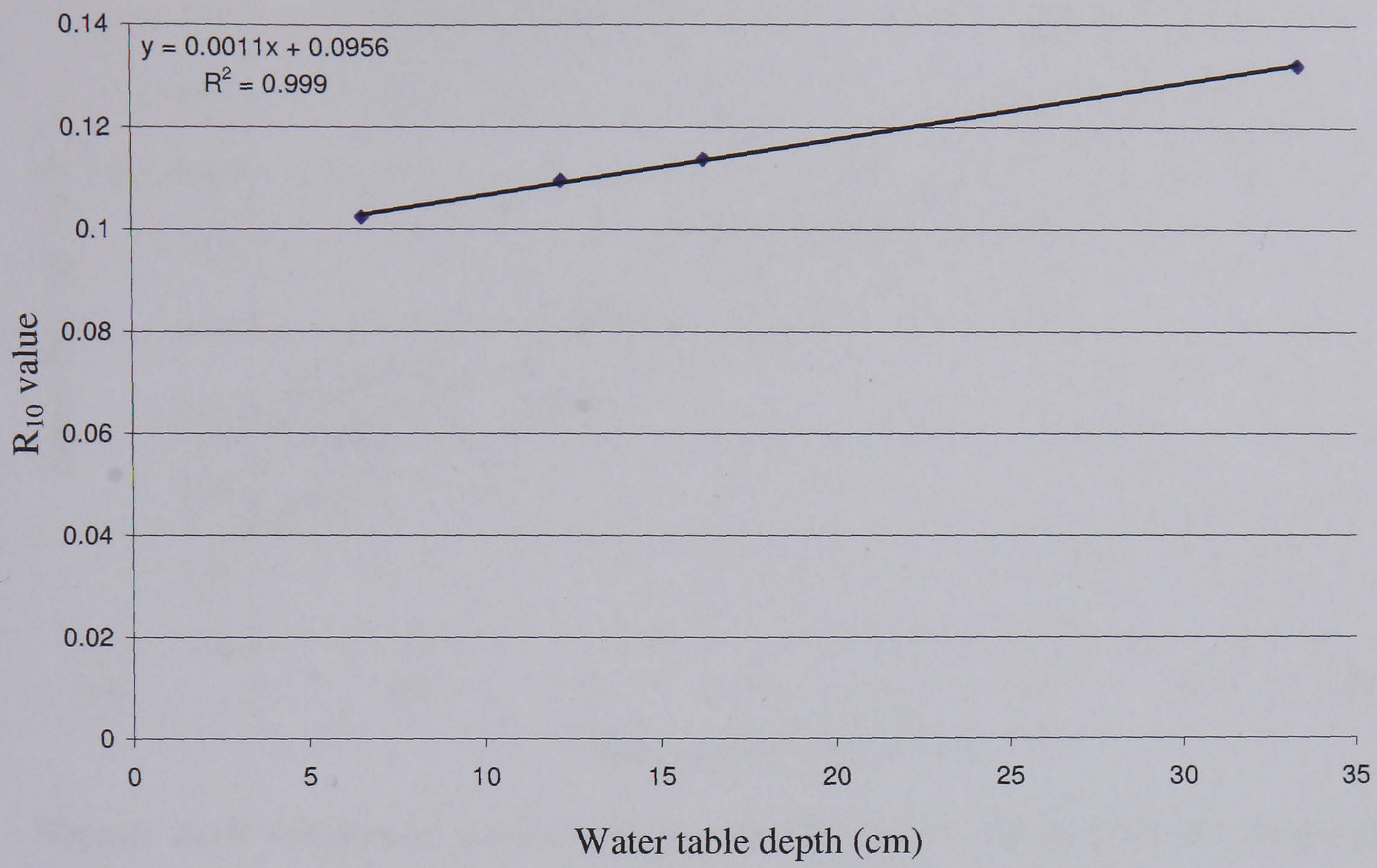

Figure 3.17 R_{10} relationship with average water table depth

As can be seen from the graph (Figure 3.17) there is a strong relationship with R_{10} values and water table depth ($P = 0.001$, $n=4$, $R^2 = 99.9\%$, R^2 adjusted = 99.8%). Applying the linear equation to the water table depth results and recalculating the Lloyd and Taylor equation to include this information, and plotting this predicted gaseous and dissolved flux against actual gaseous and dissolved flux gives the following graph (Figure 3.18)

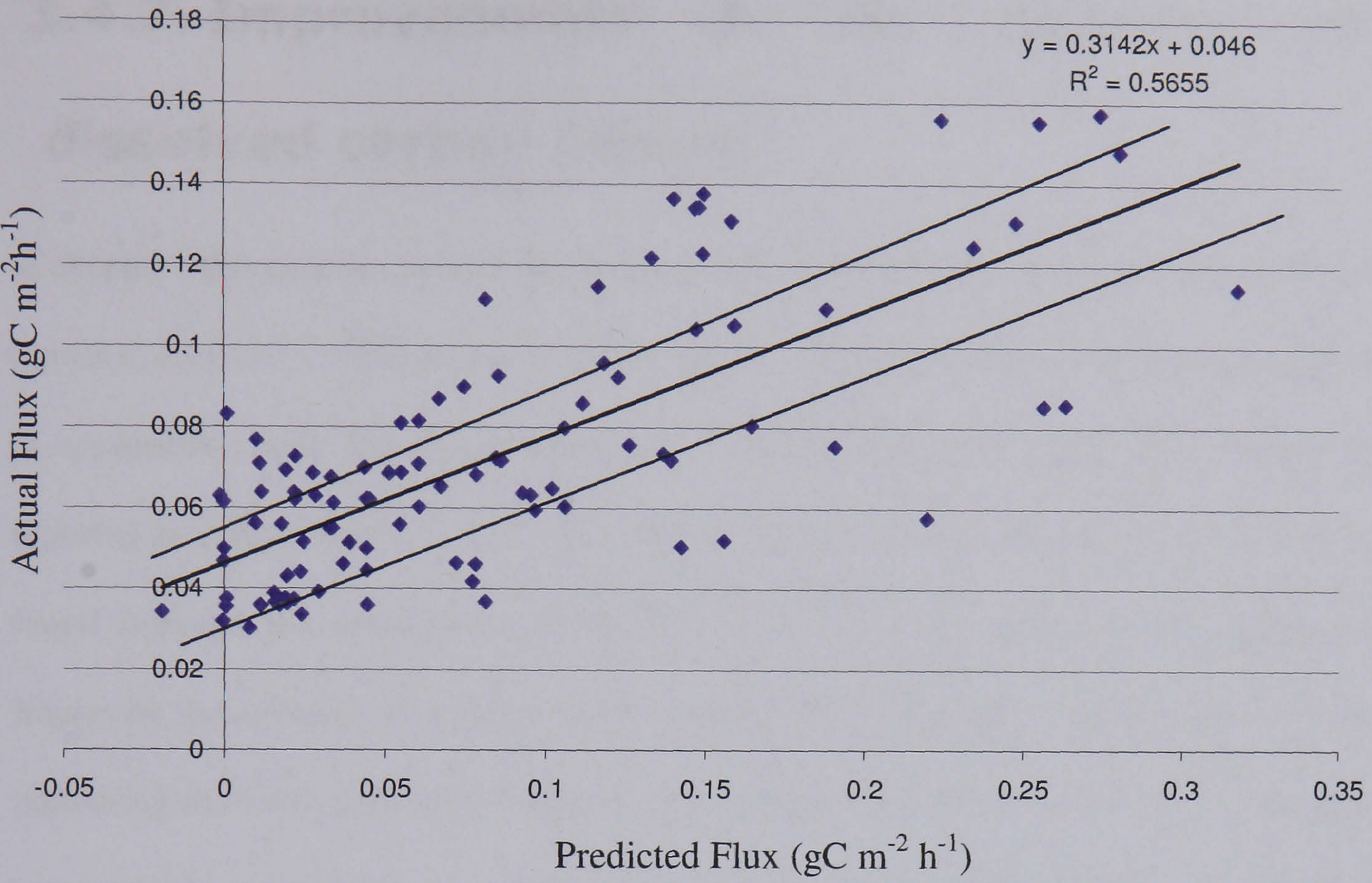

Figure 3.18 Predicted gaseous and dissolved flux against actual dissolved flux using water table depth to predict R_{10} values with best fit, maximum and minimum error lines

As can be seen from this graph (Figure 3.18), this is an improvement on previous R^2 values. To improve the relationship further the linear equation (Figure 3.17) constants (m = 0.0011 and c = 0.0956) were solved using an annealing solution to reduce the error between the predicted gaseous and dissolved fluxes and the actual gaseous and dissolved fluxes. This increased the overall $R^2 = 0.5824$, which is an improvement of 5.22% of the relationship with gross gaseous CO_2 flux and predicted gross gaseous CO_2 flux.

3.4.7. Improvements in the gaseous and dissolved carbon budget

In chapter 2 the gaseous carbon budget was reported to be a net source of carbon of 17.72 tonnes C Km^{-1} yr^{-1}. This was a best fit estimate based on the Lloyd and Taylor equation in conjunction with the Bubier equation. The total gross CO_2 flux for the site was reported as 189.91 tonnes C Km^{-1} yr^{-1}. In the previous section (Section 3.4.7) a link was found between the respiration rate at 10^0C and water table depth. This relationship improved the amount of variance explained by the Lloyd and Taylor equation, when predicting the total respiration value for both gaseous and dissolved CO_2 flux. Using the same method as in chapter 2, section 2.3.5 to predict the carbon budget for the field site based on a 15 minute data set for soil temperature and water table depth the carbon budget can be recalculated to include this relationship and improve the total carbon budget estimates for the site. Therefore the carbon budget will now include the total respiration values for the site, which will be a sum of the dissolved and gaseous gross respiration and the total amount of CO_2 taken up by the plants at the site:-

$$Carbon\ Budget = (Primary\ Productivity) + (Gross\ gaseous + gross\ dissolved) \quad \textbf{3.xxv}$$

Where CO_2 uptake is negative and CO_2 release is positive.

Collar Number	Carbon budget for each collar without R_{10} and water table depth correction (tonnes C Km^{-1} yr^{-1})	Carbon Budget with R_{10} and water table depth correction (tonnes C Km^{-1} yr^{-1})
1	-13.36	-44.40
2	154.99	123.81
3	-29.43	-47.40
4	134.91	116.94
5	-34.62	-142.46
6	226.47	118.63
7	148.33	25.16
8	243.26	120.09
Average Gross respiration	189.91	119.87
Average Primary Productivity	-172.18	-172.14
Average Carbon budget	17.73	-52.28

Table 3.9 Comparison of different carbon budget calculations

As can be seen from the table (Table 3.9) the field site has turned from a source of carbon into a sink. From the table it can be seen that, overall, the primary productivity has not changed, and the plants are still predicted to take up the same amount of carbon, however the site is now predicted to release less carbon even though this is a total carbon release

which includes both gaseous and dissolved CO_2. It can also be seen from the graph that collar 2 is predicted to release the greatest amount of carbon, and collar 4 the lowest amount of carbon, which again, like the R_{10} values follow the trend of the average water table depth.

3.5. Discussion

From the results section it has been proposed that there is a single mechanism for CO_2 production where different drivers determine;

1). How much CO_2 is produced?

2). Where the CO_2 ends up?

Thus, the following diagram (Figure 3.19) has been proposed to explain: the source of CO_2; the factors controlling the amount of CO_2 produced; and the controls of whether CO_2 is dissolved into the ground water or fluxes from the surface as a gas.

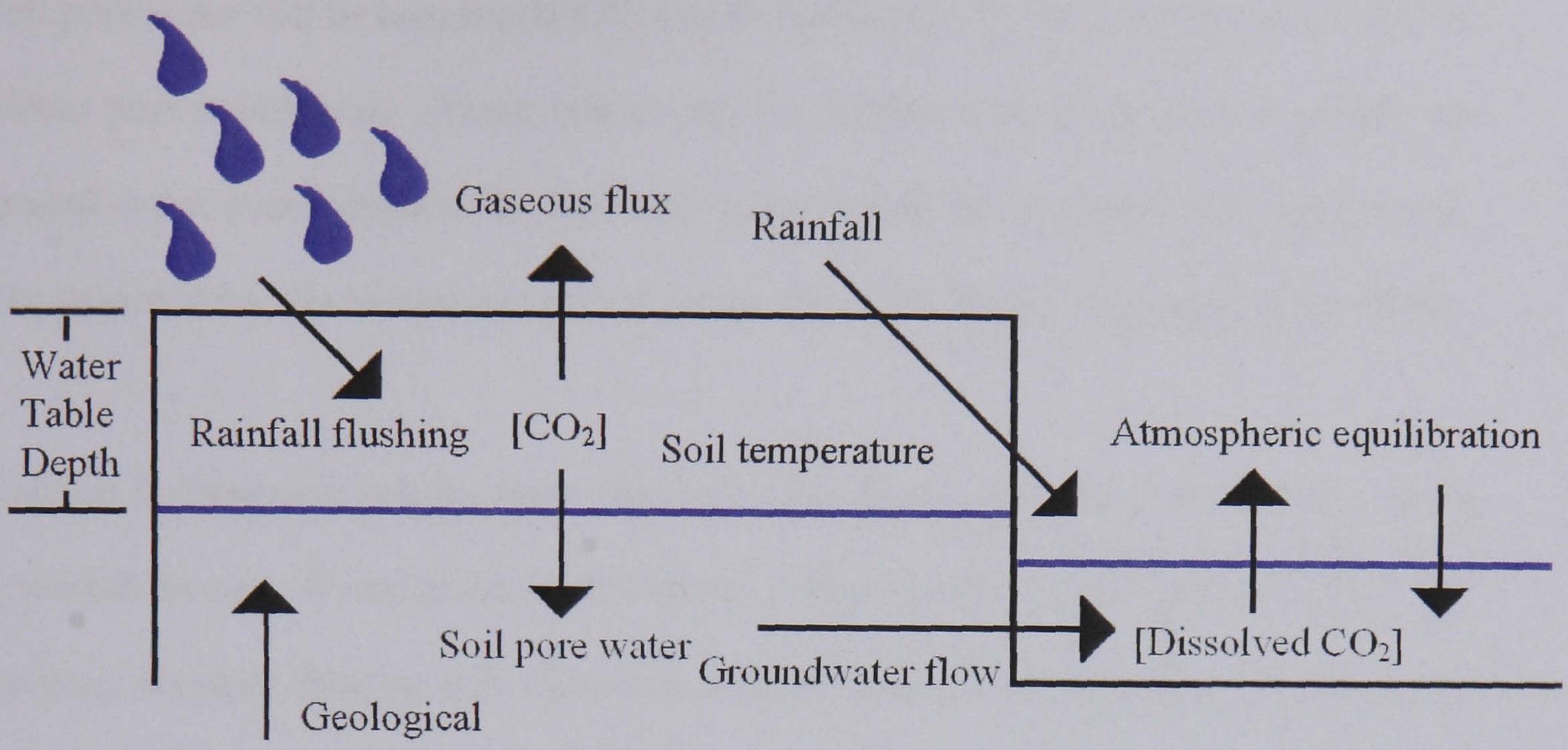

Figure 3.19 Proposed total carbon flux model

From Figure 3.19 all the terms have been defined below, and their contribution to the model and their effects on CO_2 flux are explained:-

Geological defines the amount of CO_3^{2-} inputted into the peat system from weathered calcium carbonate. The ultimate output of this carbonate ion is into the grip or stream system. A simple measure of the carbonate ions in solution used to predict the amount of dissolved CO_2 in the system may be affected by this result. In this study the calcium ion (Ca^{2+}) was measured to compensate for this. From end member mixing analysis calcium was found to be higher at low flows, suggesting a geological source, especially from Widdybank, which had much higher calcium concentrations compared to the gripped sites, and a higher pH value.

Soil pore water will be enriched in CO_2 due to equilibrium of the soil pore water with the within peat atmosphere. These waters can be flushed from the peat and provide the ground water contribution to the grip and define one of the end members of the model. The evidence for this is from Figure 3.4, where CO_2 concentration is higher at low flows.

Rainfall flushing will initially flush dissolved CO_2, Al, Ca, and DOC into the grip during a rainfall event. A sustained rainfall event will then dilute these species in the grip system. Rainfall flushing will also have a longer term effect in raising the water table depth, which will interact with CO_2 fluxes.

Rainfall will fall either directly into the grip diluting any species in solution, or will flow over the surface of the peat and have very little interaction with the peat, and will provide the second end member of the system. The amount of CO_2 dissolved in the rain water is assumed to be in equilibrium with the atmosphere.

CO_2 flux is a direct measure of the CO_2 fluxing from the peat surface. This is proposed as one of the measures needed to complete the CO_2 budget for the site.

Dissolved CO_2 is the second direct measure needed to complete the carbon budget for the site, and is a measure of the total amount of CO_2 dissolved in the grip or stream system.

Atmospheric equilibration is the fluxing of CO_2 either from the grip into the atmosphere or vice versa. In this case it is assumed that CO_2 has not degassed to a great extent from

the system as measurements were taken near the head waters.

Soil temperature is the second and most important factor in predicting the amount of carbon produced within the peat, and is a rate limiting step on the amount of CO_2 produced by the soil microbes.

From the diagram (Figure 3.19) it is proposed that there is a single mechanism for CO_2 production where the amount of CO_2 produced is defined by water table depth and soil temperature. It is then proposed that different drivers; water table depth, soil temperature, and rainfall, and rainfall flushing determine whether the CO_2 is dissolved into the groundwater system or fluxes directly from the surface as a gas. It is proposed that direct measures of CO_2 from the surface and measures of dissolved CO_2 will account for all the CO_2 within the system.

3.5.1. Validity

So is this model is a valid one? Assuming this model is correct and that there is a single mechanism for CO_2 production, which leads to a more complete total CO_2 budget, with combined dissolved and gaseous fluxes, for the field site which improved the amount of variance explained by the Lloyd and Taylor (Lloyd *et al.,* 1994) equation. From this model both soil temperature and water table depth where considered together as predictors of total flux from the field site. The amount of variance explain prior to this relationship was 53.01%. Assuming the model is correct, the amount of variance now

explained is 58.24%. Assuming this model is also correct the Lloyd and Taylor equation now has a linear function relating the R_{10} function, proposed by Lloyd and Taylor, to water table depth. This improvement allows the flux from the site to be calculated with measures of water table depth and soil temperature without the need to measure CO_2 fluxes first and solve the Lloyd and Taylor equation for R_{10}. It is unknown whether this relationship holds for other environments; indeed it is unknown whether this relationship will hold for a similar peatland. In this experiment it was assumed that soil moisture was not a rate limiting step. In another peatland this assumption would also hold, as the water table is likely to be close to the surface. Another environment, such as a forest, where there is likely to be soil moisture inhibition on the soil respiration microbes may have a different relationship with water table depth. For a forest environment, the relationship between water table depth and R_{10} may by linear until soil moisture starts to become a rate limiting step to the soil microbes, then the Lloyd and Taylor may over predict fluxes at high temperatures. This may not be too much of a problem because the Lloyd and Taylor equation tends to under predict fluxes at high temperature, and normally when there is high temperature there will be a deeper water table depth, so if the fluxes are slightly over predicted then this may, in fact, provide a better fit then found here.

How valid is the assumption that R_{10} will vary with water table depth? R_{10} is defined by Lloyd and Taylor (1994) as the amount of respiration of any environment at 10^0C. Therefore, what are the factors that affect respiration within soils? It is commonly know that there are 3 limiting steps for soil microbes; temperature, nutrients, and soil moisture. In this study it is assumed that soil moisture is not a limiting step. Therefore, the two

remaining limiting steps are temperature, which has been accounted for within the Lloyd and Taylor equation, and nutrients. In this study oxygen can be classified as a nutrient because the amount of oxygen in the peat will be defined by the depth of the aerobic zone and the rate of diffusion through the peat. In addition, an upland peat environment is extremely poor in nutrients being supplied only by the nutrients dissolved in rainwater. Other nutrients within the peat may also provide another rate limiting step to the microbes, and if these were measured may increase the amount of variability explained. The main source of nutrients within the peat profile is likely to have come from plant root exudates, which is likely to be higher in summer than winter, and may provide a further explanation of the variance within the peat CO_2 flux.

The linear equation used to predict the R_{10} values in relation to water table depth can, theoretically, be used to describe the substrate further. The intercept value (c) can provide information on either the amount of CO_2 contributed by the anaerobic zone to the total CO_2 flux by anaerobic decay which is stated as 50 times slower than aerobic decay (Clymo, 1983). This value can also provide information on than the amount of oxygen diffusing below the water table and oxidising either methane or available carbon, which is unavailable to the anaerobic microbes, via either microbial or chemical processes. The gradient (m) of the linear equation can provide information on the microbial community within the aerobic zone, where different microbial communities will produce CO_2 at different rates, thus these different rates can be used to define different communities.

In studies that have used the Lloyd and Taylor equation to predict the gross flux for the

site by measuring CO_2 fluxes on a campaign basis and using data loggers to record soil, and air temperatures, water table depth, PAR, rainfall, and other environmental measures have found that water table depth to be insignificant in regression analysis (Lloyd, 2001, 2000; Qi *et al.*, 2002; Lloyd *et al.*, 1994; Chapman *et al.*, 1997). All of these studies assumed that there was no limitation in the soil moisture levels. Arneth *et al.*, 2002 used eddy covariance measurements on Siberian peat, and fitted the measured data to the Lloyd and Taylor equation and from that data predicted the R_{10} value for the site. Arneth noted that when the flux data was grouped into monthly bin averages and R_{10} values calculated, the R_{10} values were lowest in spring and highest in summer. Arneth also noted that this was probably due to decreased water table depth, increased temperature and increased productivity, and it was further noted that Arneth did not measure water table depth, but observed that the free water surface area declined considerably as summer evaporation exceeded precipitation. Other studies reporting values of R_{10} (Flanagan *et al* 2005; Arneth *et al.*, 2002; Lloyd 2001; Glenn *et al.*, 2006; Bergeron *et al.*, 2007) reported R_{10} values between 0.01631 (Lloyd, 2001) – 1.1014 (Bergeron, 2007) $gCO_2\ m^{-2}h^{-1}$. In the literature a study that measured soil respiration and found a relationship to water table depth was Lloyd (2006). The study was performed on a managed wetland meadow on the Somerset levels. The study used an eddy covariance method to measure net CO_2 flux, assuming soil respiration measurements to be equal night time measures of net CO_2 flux. The linear equation was;

$$0.000747958187 \times \textit{Water Table Depth} + 0.19765809274 \qquad \textbf{3.xxvi}$$

NB. This equation differs from the equation reported in the Lloyd (2006) paper as the

units have been converted into $gCO_2\ m^{-2}h^{-1}$ rather than the units used in the Lloyd (2006) paper, which where $\mu molCO_2\ m^{-2}s^{-1}$.

This equation has much higher gradient (m) and intercept (c) values, which would suggest that the rate at which CO_2 is produced (m) is greater, and the amount of initial CO_2 produced (c), thought to be the contribution by anaerobic respiration is also much higher. A reason for this could be that this study only considered the gaseous fluxes from the site. The site is 'a very broad flat floodplain approximately at sea level, criss-crossed by an extensive network of drainage ditches' therefore CO_2 will be exported from the site as dissolved CO_2 as well as gaseous CO_2, which has been shown in this study to have the same production mechanism as gaseous CO_2. Using an eddy covariance method to measure the fluxes from an intensively drained site will include a measure of the degassed CO_2 flux directly from the drainage system, so a proportion of the dissolved gaseous flux will be captured depending on the drainage density and position of the flux tower. It is therefore proposed that the c constant in the equation could be a measure of the 'lost' CO_2 exported as dissolved CO_2. The greater production rate of CO_2 (m) from the equation could represent a different microbe community compare to the microbe community measured here as the environment studied here is an upland peat, in the North of England, whilst the Lloyd (2006) study is a lowland study in the South of England.

The amount of error in calculating the dissolved proportion of the total flux calculated by Neal *et al* (1998) to be 1.5%. It is therefore assumed that the CO_2 calculated here is a good estimate of the actual CO_2 flux for the stream.

This prediction of the total CO_2 budget for an upland peat is specific for this type of upland peat: an upland peat close to the head waters that has been heavily gripped and is a flashy in response to rainfall.

3.5.2. Implications

What are the implications for a soil respiration linked to water table depth? Studies that have used a constant R_{10} value to predict the total respiration for a site may have underestimated CO_2 fluxes during the summer months when water table depths are generally lower and over estimated the carbon fluxes in winter when water table depths were high. For an upland peat that is predicted to be a sink of carbon, currently having a high water table depth during winter months, with low respiration and very low carbon uptake, and having a deeper water table depth during summer leading to higher gross carbon fluxes. So how will this flux values be affected by global warming? Global warming is predicted to reduce the amount of rain during summer months and increase the amount of rain during winter months. The implications of this are that overall an upland peat will receive the same amount of annual rain only at different times of the year. This will mean that although the peat will have a high water table depth in winter, with the corresponding low fluxes, the lower rainfall in summer will mean deeper water table depths. According to this proposed relationship between R_{10} and water table depth in the Lloyd and Taylor equation an increased water table depth in summer combined with the corresponding high temperatures would predict greater amounts of carbon

released from the peat surface. The potential for this could mean that sensitive peat could turn from a sink of carbon to a source thus creating a positive feedback loop increasing the levels of CO_2 in the atmosphere, and increasing global temperatures drying the peat further.

This is a significant result because if R_{10} is linked to water table depth then there is a relationship between the total amount of CO_2 produced and water table depth. This relationship was not found in chapter 2, where it was concluded that there was no relationship between water table and gross CO_2 flux. This results also suggest that there is indeed a single mechanism of CO_2 production and soil temperature and water table depth define how much is produced and where the flux will emerge from the peat system. Hope *et al.,* (2004) examined the relationship between dissolved CO_2 and gaseous CO_2. The Hope *et al.,* (2004) study measured the concentration of CO_2 and CH_4 not the flux values. In the study it was found that there were significant relationships with; soil and air temperature, stream flow, and a lagged delay between the concentration of CO_2 in the peat soil. The aim of the Hope study was to use CO_2 concentrations in the streams as a proxy for the gaseous respiration for the catchment, considering total respiration to calculate the carbon budget for an upland peat was not a factor considered.

This understanding of the relationship with soil temperature and water table depth may aid with the restoration of upland peat. Some studies have concluded that there is a relationship with water table depth and the amount of CO_2 flux from the peat surface (Tenhunen *et al.,* 1995; Baldocchi; Hunt *et al.,* 2002; Wessolek *et al.,* 2002; Hashimoto *et*

al., 2006; Lloyd, 2006; Blodau *et al.*, 2004; Bubier *et al.*, 2003), whilst others have concluded that there is no relationship between water table depth and respiration (Bridgham *et al.*, 1991; Updegraff *et al.*, 2001; Nieveen *et al.*, 2005). It could be that CO_2 production has not been considered as a single mechanism for carbon production, and have not considered the combined dissolved and gaseous flux and concluded, as was thus found in chapter 2, that there was no relationship between the CO_2 flux and water table depth. Other studies did not need to consider the relationship with water table depth because of retarded ground water flow in a pristine peat with little drainage, natural or otherwise, and a stable water table depth, where a simple constant R_{10} value would suffice. Other studies found that water table depth to be significant, in these studies there was little drainage, so little CO_2 would be lost as dissolved CO_2 and most CO_2 would have fluxed from the peat surface as a gas.

In this study it can be said that the restoration of the water table depth will reduce the amount of carbon being produced because of the relationship found with R_{10} and water table depth. However, the reduction of grip flow will also reduce the amount of carbon being lost from the peat because rainfall acts to flush the CO_2 produce within the soil pore space and equilibrated with the within peat atmosphere with the soil pore water.

The composition of the stream water chemistry can also be based on this model. Where rainwater and soil pore water will mix in different proportions to create the stream chemistry. The factors affecting the stream chemistry from statistical analysis are flow, rainfall, conductivity, and log of conductivity and flow. These relationships led to the

classification of two, two end member stream systems; Widdybank and the gripped systems. In this system there are two main sources of input into the system, geological, and precipitation, these are then modified by within peat processes, such as respiration, soil temperature and water table depth. Rainfall affects the pH, conductivity, aluminium, and calcium values of the grip or stream. All of these variables are interconnected, with conductivity being a proxy of the total dissolved species within the stream, pH is affected by rainfall by diluting the soil pore water as rainfall has a much high pH than the soil pore water, rainfall also has a much lower conductivity than soil pore water, and so conductivity will decrease with rainfall. Aluminium and calcium are affected by rainfall by being flushed from the system during rainfall events, and are related to conductivity by being one of the dissolved species in solution.

So how is stream chemistry affected by the different treatments? From a plot of gran acidity and alkalinity over time it can be seen that there are clear differences in the gran acidity and alkalinity between the different treatments. Widdybank has a much higher charge value then the Cowgreen site, whilst the Hexhamshire Common results have values in-between these two extremes, with Hex 2 having higher values than the two blocked grips. From the changes in gran acidity and alkalinity the pH compared to conductivity was looked at (Figure 3.10), and it was found that the pH was relatively stable for all sites, with Widdybank having the highest pH values, and Hex 2 having the lowest. The main control on the pH of the site is the amount of rainfall the site receives with pH being increase for the gripped sites with rainfall and the pH being reduced for Widdybank fell, having a different chemical makeup.

The high levels of calcium in the Widdybank Fell stream are much higher than in the other drainage systems (See Table 3.7). The most likely explanation for this is that further upstream of the sample site the stream flows over an outcrop of limestone. This would account for the high levels of dissolved calcium in the stream and the much more neutral pH values when compared to the other drainage systems. This led to the conclusion that the geology underlying Hexhamshire Common and Cowgreen sites was not a contributing source of carbonate, and thus any calcium in the drainage waters came from meteorological sources. It was also concluded that Widdybank Fell was underlain by a carbonate source, and thus the calcium levels were much higher than the other sampling sites.

3.5.3. Gaseous and Dissolved Carbon Budget

In calculating the total carbon export for each grip it was found that Hex 1 at the Hexhamshire Common field site has the second lowest carbon export figure of all the measurement sites. Yet, being a blocked grip it should have comparable export levels to Hex 3 at the Hexhamshire Common field site, and the old blocked grip at Cowgreen site. The reason for this seemingly low export figures could be that Hex 1 ran dry during summer months. It has been proposed that reducing flow will reduce the carbon export of dissolved CO_2. Stopping the flow will eliminate the possibility of any carbon being exported via the drainage system. This is supported by the fact that the grip with the greatest flow and the greatest export of carbon was Hex 2 with an export of 18.667 gC m^{-}

$^{2}a^{-1}$. However the drainage system with the lowest export of carbon was Widdybank Fell, with an export figure of 5.881 gC $m^{-2}a^{-1}$. This stream has the highest flow, but it has been proposed that the substrate at Widdybank Fell is either more stable than the Hexhamshire site, or has less labile carbon, and therefore exports less carbon or has a larger area and so dissolved CO_2 will be able to degas before samples were collected, whereas the samples for the gripped sites were collected much closer to the source of the grip.

From a combination of the dissolved and gaseous CO_2 fluxes it can be seen that the Hexhamshire Common field site is a sink of 52.28 tonnes C a^{-1}, making the field site a sink of carbon.

The export of dissolved carbon from these drainage systems is above the national average of 5.3 gC $m^{-2}a^{-1}$. A reason for this could be that upland peat environments have a soil with a much greater proportion of carbon per unit volume than the average UK soil. This would mean that it is unsurprising that they export a great quantity of carbon than the average stream.

When these results are compared to literature values it was found that an organic rich soil located 56 Km west of Aberdeen had a dissolved carbon evasion of 14.1 gC m^{-2} a^{-1} (Hope *et al.,* 2001), which is directly comparable with the Cowgreen export figure of 14.286 gC $m^{-2}a^{-1}$. Worrall (2003) reported values of 40-70 gC $m^{-2}a^{-1}$ based on a speciation method. The Worrall (2003) site was similar to the sites used in this study, with the site (Moor

house) being located less than 3 miles west of the Cowgreen site. As can be seen from the values of the Worrall study they were much greater than the values reported here (5.881 to 18.667 gC m^{-2} a^{-1}).

3.5.4. Improvements in the gaseous and dissolved carbon budget

In determining whether there was a constant mechanism of CO_2 produced within the peat and whether different driving functions, such as water table depth determined whether the CO_2 was released as gaseous CO_2 or dissolved into the drainage system to degas further downstream it was found that there was a relationship between the R_{10} values from the Lloyd and Taylor equation and water table depth. This relationship suggested that there was a positive linear relationship between water table depth and R_{10} values, meaning the deeper the water table depth the greater the amount CO_2 released at 10^0C and the shallower the water table depth the less CO_2 released at 10^0C. This is a significant relationship and a reasonable one as it was hypothesised in chapter 2, section 2.2 that there would be a relationship between water table depth and the amount of CO_2 produced with the deeper the water table depth the more CO_2 produced. This however was not that case and no relationship could be found either graphically or statistically in chapter 2. In combining the dissolved and gaseous flux, and iteratively solving the Lloyd and Taylor equation to predict the R_{10} values for each collar it was found that water table depth was significant. Using this relationship between R_{10} and water table depth to recalculate the carbon budgets using the same methods as used in chapter 2, section 2.4.5.3 it was found

that the total carbon export for the site was reduced from 189.91 tC Km^{-2} a^{-1} to 119.87 tC km^{-2} a^{-1}. This reduction in the amount of carbon released is unexpected as this budget is a combination of dissolved and gaseous fluxes, whereas the previously calculated budget was calculated on gaseous fluxes alone, therefore it would be expected that the amount of CO_2 produced would be greater than the amount produced by gaseous fluxes alone. When previously calculating the gaseous carbon budgets, each gross collar had an individual R_{10} value however using this new relationship between water table depth and R_{10} value this unifies the R_{10} relationship with gross flux. The implications of this are that the fluxes for a heavily drained site should now be comparable with a site which has not been drained. Other studies (Wessolek *et al.,* 2002; Hashimoto *et al.,* 2006; Lloyd, 2006; Blodau *et al.,* 2004; Bubier *et al.,* 2003; Tenhunen *et al.,* 1995; Baldocchi; Hunt *et al.,* 2002) have reported that water table depth affects the gross flux, and have quantified this with constants (R_{10} in the Lloyd and Taylor equation), however water table depth has not been integrated into the Lloyd and Taylor equation before. Interestingly when multiple linear regression is applied to either gaseous gross flux or dissolved gross flux summed with gaseous gross flux water table depth is insignificant as a variable. A reason for this could be that in trying to predict the best gaseous or dissolved fluxes by iteratively solving for R_{10} removed the effects of water table depth from the variability in the flux data. It should be noted that there is a difference between water table depth and soil moisture. In this experiment it is assumed that soil moisture is not a rate limiting step, and that the depth to water table affects the respiration by increasing the aerobic volume of the peat, and does not affect the rate at which CO_2 is produced.

3.6. Conclusions

3.6.1. Controls on CO_2 concentration

Looking at the different controls on the concentration of CO_2 dissolved in the drainage water, it was found that flow regime or treatment was related to the amount of CO_2 released. With the natural stream at Widdybank Fell having the lowest concentration of CO_2 in solution, with the unblocked grip, Hex 2, having the greatest concentration of CO_2 in solution, the blocked grips had the lowest concentration of carbon for all the grips. Season was also found to have an effect on the concentration of CO_2 in solution, with there being a seasonal high concentration of CO_2 in solution during summer, which decreased in winter. It was also found that pH was relatively stable throughout the year, with a slight increase in pH values over summer (More alkali) and a decrease of pH during autumn and winter months (More acidic). The most striking difference in pH between the different treatments was the pH of Widdybank Fell, which had an average pH value of around 7, suggesting that the Widdybank Fell site was chemically different from the other sites.

It was found that there was an increase in concentration of CO_2 during lower rainfall periods, and low flow periods. This was attributed to a flushing effect with 'new' rainfall flushing out the 'old' soil pore water. The greater the rainfall event, and thus the higher the flow events, the more diluted this 'old' soil pore water became until a plateau was achieved. The implications of this are that a large storm event will have a large effect on

the amount of carbon being exported from the system as although the overall CO_2 concentration will be diluted the total amount of carbon exported will much greater than a small rainfall event.

The buffering capacity of the different grips changes over time with the grips at Hexhamshire Common having an overall decrease in their buffering capacity over the year which is overlaid by a seasonal trend which increased the buffering capacity in summer and decreased in winter. The buffering capacity of the field site at Cowgreen Reservoir is much lower than the buffering capacity at Hexhamshire Common, and with the overall decrease in the buffering capacity it is thought that the buffering capacity at Hexhamshire Common will continue to decrease until it reaches similar levels to the Cowgreen Reservoir site. This is a reasonable assumption as other values such as calcium, aluminium, and pH were at comparable levels.

From the statistical analysis of the results it can be seen that flow, conductivity, average daily rainfall, log of flow, log of conductivity and treatment were all significant at the 95% confidence interval. In conclusion, the amount of CO_2 dissolved in the drainage system is related to the amount of water in the drainage system, and as conductivity is significant, the concentration of CO_2 in the water accounts for a large proportion of the total amount of dissolved species. It has been shown that treatment is also significant, and it has been shown that the greater the flow in a grip the greater the amount of total carbon will be exported.

3.6.2. Geological or peat based source of CO_2?

In conclusion it has been shown that the main source of dissolved CO_2 at the Hexhamshire Common field site and the Cowgreen site comes from the peat itself, whilst the Widdybank Fell site has an underlying carbonate source supported by the high concentrations of calcium in solution and a higher pH than the two other field sites.

3.6.3. Dissolved Carbon Budget

It has also been shown that the release of dissolved carbon is always positive. This means that upland peat is a net source of dissolved inorganic carbon. The amount of carbon lost by an upland peat system depends on a number of different factors, with the main factors being conductivity and average daily rainfall (See Table 3.1).

The largest exporter of carbon from all five measurement sites was the unblocked grip, Hex 2, at Hexhamshire Common, with an export of 18.667 g m^{-2} a^{-1}. Three of the five sites were blocked grips with two being blocked in 2003 and one blocked in 1995, and their export values were similar ranging from 10.556 to 16.667 g m^{-2} a^{-1}.

In comparing the gaseous carbon budget and the dissolved carbon budget is can be concluded that the dissolved CO_2 flux is comparable to the gaseous CO_2 flux with the average dissolved CO_2 flux for the site being 17.667 gC m^{-2} a^{-1} whilst the gaseous CO_2 flux was 17.73 gC $m^{-2}a^{-1}$. When scaled up over the area of the field site it was found that the field site was a net producer of gaseous and dissolved CO_2 of 0.3504 tC a^{-1}.

3.6.4. Improvements in the gaseous and dissolved carbon budgets

It was found that there was a relationship between water table depth and R_{10} values for the site allowing a scaling R_{10} to be applied over the year in relation to water table depth. This may be a false relationship overlaying a seasonal trend however it is reasonable to conclude that the Lloyd and Taylor equation may have a water table component, which would relate to the aerobic volume of peat. Many literature sources have concluded that there is a relationship between water table depth and soil respiration. It is also reasonable to conclude that there is no relationship between R_{10} and soil temperature because of the very definition of the R_{10}. This relationship could provide a greater understand of the microbial processes within the peat, and in other soil types. When recalculating the carbon budget, using the same methods as chapter 2, it was concluded that the peat was a sink of carbon, this was caused in the reduction of the relative R_{10} values. The overall carbon budget for the site is now calculated to be -52.3 tonnes C Km^{-2} a^{-1}.

3.6.5. Further Experimentation

Several dissolved CO_2 measurements could be taken over a single day. This would allow the diurnal variations to be accounted for, which may change the proposed carbon budget values.

Another experiment could take water samples from different locations down the length of the drainage system. This would look at the change in concentration of CO_2 down the streams length. This could also provide information on the mineralisation rates of DOC to CO_2. This information is useful in water treatment as DOC is expensive to remove and may cause potential carcinogenic by-products if not chemically removed fully.

If this potential relationship between R_{10} values and water table depth is correct then further experiments would be need to confirm whether this relationship could explain the CO_2 release from none drained peat, and other drained peat sites. If the hypothesis is correct that the gradient of the linear equation (m) represents the different microbe community within the peat, this could be applied to other soil communities. Again, if the hypothesis that the intercept value of the linear equation (c), represents the contribution from the anaerobic zone, then this could be tested by applying the formula to dry soils or soils with a deep water table depth, where the intercept should be zero.

4. Chapter four: Carbon Dioxide Release from Peat Cores

This chapter takes a series of deep peat cores from an upland peat and relocates them to lower altitudes which will increase temperature and reduced rainfall with the aim of simulating the effects of climate change on the CO_2 fluxes from an upland peat.

4.1. Introduction

4.1.1. The problem of climate change?

Global temperatures increased by about 0.6^0C over the last 100 years, with 1998 being the warmest single year on record (Hulme *et al.*, 2002). In the UK, the climate has changed consistently with global temperature changes, with parts of central England having a 1°C temperature increase during the twentieth century (Hulme *et al.*, 2002). Winter across the UK has been getting wetter, with a larger proportion of the precipitation falling in the heaviest downpours, while summer have been getting slightly drier (Hulme et al., 2002). In recent times there has been a large emphasis on how different environments will respond to climate change, especially more climatically sensitive carbon stores such as upland peat located on the southern limits of peat growth. It has been hypothesised that these environments can be used as either; a predictor of the effects of climate change on more northerly peat (Ellis *et al.*, 2000) or; can be used as an

'early warning system' on the effects of climate change (Bonnett et al., 2006 and Aerts 2006). The UK is estimated to have an increase of between 2 and 3.5°C by 2080's, with general warming occurring in the South East to a greater extent than in the North West. It is also predicted that annual average precipitation will slightly decrease between 0 – 15%, although it is noted that there are likely to be large regional and seasonal differences (Hulme et al., 2002).

Climate change is caused by increased concentrations of greenhouse gases in the atmosphere. The main greenhouse gas in the atmosphere, by weight, is water vapour and is naturally occurring, the second and most significant is CO_2 and the third is CH_4. All of these gases absorb the long wavelength emitted by the earth and prevent it being emitted back into space, thus increasing average global temperatures. By 2080's the UKCIP02 climate change scenarios predict an increase of CO_2 ppm concentrations between 525 and 810 (Low emissions scenario, and high emissions scenario respectively) representing an average increase of two to three times pre-industrial concentration of 280 ppm (Hulme *et al.*, 2002).

The Government is regulated under the ratified Kyoto protocol to reduce the UK's emissions of the main greenhouse gas: CO_2. Several schemes are in place to reduce CO_2 emissions from industry, however the government is also interested in natural, managed sinks of carbon. A large sink of carbon in the UK is upland peat, storing an estimated 0.7 MtC a^{-1} (Cannell *et al.*, 1999). Therefore, there has been much interest in how these climatically sensitive environments will respond to increased temperatures and reduced

rainfall predicted for the UK by the UKCIP02 report (Hulme *et al.*, 2002).

There are two potential methods for predicting the effects of climate change on upland peat. The first is an extrapolation method which takes measurements of CO_2 fluxes from upland peat and relates CO_2 fluxes to driver variables such as soil temperature and PAR, and then estimates a temperature increase for the peat and extrapolating the relative increase in CO_2 release (Fronzek *et al.*, 2006; Lloyd *et al.*, 1994; Yu *et al.*, 2001a). The second method is to take peat cores from upland peat and move them to a location of increased temperature and reduced rainfall to simulate an increase in global temperatures and simulate a change in local weather patterns (Yu *et al.*, 2001b). The approach taken by this study was to extract a series of deep peat cores from an upland peat and move them to lower altitudes. By moving to lower altitudes this study increases temperature approximately 1°C for every 100m decrease in height. This increase in temperature will simulate an increase global temperature. Increasing the average temperature of the peat cores will increase the amount of evapotranspiration from the peat cores. This will reduce water table depth of the peat cores, and it has been found in other studies (Savage *et al.*, 2001) that there is a link between the water table depth and the amount of CO_2 fluxing from the peat surface. Durham City, where the peat cores were located is situated in the rain shadow of the Pennines, and receives less rainfall than the Hexhamshire Common field site; the water table depth will be controlled by draining, simulated and natural rainfall.

Worrall *et. al.* (2005) found a link between DOC production from upland peat and

drought conditions; this has been linked to an enzyme latch mechanism (Freeman *et al.*, 2001) which keeps the amount of DOC produced at higher levels than would be expected once the water table depth has been restores to pre-drought levels. As has been demonstrated by DOC trends, the carbon cycle from upland peat has been disturbed by drought conditions. Therefore, a simulated drought on a series of deep peat cores may show an increase in the amount of CO_2 fluxing from the surface of the peat, post-drought, that cannot be explained by the driver variables which predict net, gross, and primary productivity CO_2 fluxes, as has been found by DOC trends

4.2. Objectives and Hypothesis

The objectives of this study are:-

1. To determine the effect of increased temperature on net, gross and primary productivity CO_2 fluxes

2. To determine the effect on net, gross, and primary productivity CO_2 fluxes by lowering the water table

3. To determine the effect on net, gross, and primary productivity CO_2 fluxes by increasing the height of the water table

4. To determine if the CO_2 fluxes measured from peat cores moved to a lower altitude with higher temperatures and lower rainfall are comparable to the fluxes measured at the field site from where the peat cores were extracted.

4.3. Methods

4.3.1. Field Site description

Six peat cores were extracted from Hexhamshire Common field site. For a full description of the field site see Chapter 2 Section 2.3.1.

4.3.2. Experimental design

Six peat cores were extracted using 80cm length 15cm diameter UPVC waste pipe. The extraction method involved placing the cores onto the surface of the peat and cutting through the vegetation layer of the peat around the cores, and the pushing the cores to depth as quickly as possible. The edges of the cores were filed to an edge to aid with cutting the peat core, and to minimise compaction. The amount of compaction of the peat core was recorded. The cores were also cut during the winter when the surface layer of the peat was frozen. This was done with the aim of keeping as much of the structure of the peat intact as possible, ensuring that microbial activity was at a minimum, and the water table was at its maximum level. There were concerns that whilst extracting the peat cores, most of the cores would be below the water table and the resulting hole would quickly fill with water making extraction impossible. As the peat cores were being extracted there was little water in the hole, just damp peat, and towards the end of the core extraction there was a little water seeping down the sides of the hole. There was a concern that extracting the peat this way would lead to the peat becoming aerobic, but as there was little water loss from the side of the hole whilst the peat cores were being

extracted, it was assumed that very little of the peat core became aerobic.

Figure 4.1 Peat cores being removed from the peat with a little water seepage in the bottom of the hole

The peat cores were sealed with pressure caps used in the water industry to stopper waste pipes. This involved a short (~30cm's) length of pipe slightly wider in diameter than the core pipe and was fitted with two rubber flanges which gripped the sides of the core tube to provide a water and gas tight seal between the side of the core and the sealing collar. The base of the short tube was sealed with a flat piece of plastic which fitted onto the

base of the sealing collar again providing a water and gas tight seal, and can be seen in Figure 4.2 at the base of each peat core. A piezometer tube was fitted to each core. This was achieved by modifying a suba seal™, a gas tight seal, and fitting a clear 5mm diameter through the middle of suba seal™ and extending 7cm beyond the suba seal™ the clear 5mm plastic tube beyond the end of the suba seal™ was holed in several places to allow faster equilibration with the soil pore water within the core. A 15mm hole was then drilled at the base of each core above the sealing collar and the modified suba seal™ with the clear tubing used to stopper the hole. The clear plastic tube was then extended to the top of the peat core. This tubing, after a period of time, equilibrated with the water table depth within the core due to hydrostatic head equilibration. This piezometer tube was then used to control the water table depth by allowing the core to drain freely to a certain depth. The water table depth was measured as the depth below the surface of the peat, and the water table depth was controlled by moving the piezometer tube to 10, 20, 30, 40, and 50 cm's below the surface of the peat core and allowing the water to drain freely out of the piezometer tube. The piezometer tubes can be seen in Figure 4.2 running up the side of the peat cores, and the depths below the water table can also be seen in this figure.

Figure 4.2 Peat cores outside department with sealing caps on the bottom, and piezometer tubes measuring water table depth

Figure 4.3 Peat core at the end of experiment showing a range of vegetation still alive suggesting the extraction method maintained root structure and pore spaces

It was thought that the peat would dry slightly and move away from the edge of the drainpipe quickly drying the peat out and forcing the peat to become aerobic. However whilst installing a piezometer to measure the water table depth, a small hole was drilled into the side of the core and when the plastic was puncture there was a small hiss of gas release. If the core were in atmospheric equilibrium, then there would have been no gas release. There was also concern that the sides of the core would act as macropores within the peat, and homogenising the water within the core. As the water table was reduced in depth by draining the water table from the bottom, the hydraulic conductivity of the peat

could clearly be seen by the rate of water flow, and if the sides of the cores were acting as macropores then the peat cores would drain any free water from within the peat cores at a much faster rate than was seen. Another factor, which led to the conclusion that the peat cores were hydraulically stratified, was the colour of the water removed. The water removed was clear to slightly brown, much lighter than ordinary water sampled from grips at Hexhamshire Common field site, suggesting that the peat is acting as a filter for DOC and POC, and if the cores had been acting as macropores then the water colour would have been similar to drainage water sampled from Hexhamshire Common field site.

4.3.3. Gas Flux measurements

The concentration of CO_2 being released from the peat cores was measured with an IRGA (Infra-Red Gas Analyser PP-System EGM-4, Hitchin, UK) in conjunction with a purpose bought environmental chamber from PP-systems (CPY-2 Closed chamber system PP-systems, Hitchin, UK) which measured the ppmv concentration of CO_2 within a known headspace volume. The water table depth was kept constant by a piezometer tube running from the bottom of the lysimeter, and allowing any excess water to drain and topping the water table up with collected rainwater (See Figure 4.2). Flux measurements of net CO_2 and gross CO_2 were taken on Monday to Friday at the same time each day (between 2pm and 3pm). Every Friday for five weeks the water table piezometer tube was moved 100 millimetres towards the base of each core relative to the surface of the peat core. This allowed the cores to drain freely until the water table was in equilibrium with the piezometer tube. The water table depth was taken down to a total

of 500 millimetres below the peat surface which took five weeks. The water table was then allowed to raise both naturally and artificially. Rain water was collected both during the period of water table reduction and water table rise. This rain water was then frozen after each rainfall event, and then used to raise the water table depth in conjunction with natural rainfall. It was aimed to raise the water table by 100mm a week, with both rainfall and collected rain water however this was not always practical as not enough rainfall could be collected and July of 2006 was the hottest July on record. Measurements were taken between 27/04/2006 and 20/07/2007, and in total 608 measurements were taken.

4.3.4. Climatic measurements

The purpose built chamber for the IRGA had a series of environmental instruments which were recorded and formed the driver variable data set for this experiment. The variables measured were air temperature, PAR, and atmospheric pressure.

4.3.5. Statistical analysis

Multiple Linear regression and ANOVA was used to test the statistical significance of the data collected. For a full description of multiple linear regression and ANOVA see chapter 2 section 2.3.7

4.3.6. Modelling

Briefly, modelling of carbon fluxes over time will follow the approach set out in chapter 2 section 2.4.5.1. This approach uses two literature defined equations from Lloyd and Taylor, (1994), to define gross CO_2 flux based on soil temperature, and Bubier *et al.*, (1998) equation to predict net CO_2 flux based on PAR and substituting the Lloyd and Taylor equation into the Bubier equation. The Lloyd and Taylor equation will also be modified to include the improvement proposed in chapter 3.

4.4. Results

4.4.1. Effects of increased Temperature on CO_2 fluxes

Fluxes were divided into three different categories, net flux, gross flux and primary productivity flux where for the sake of completeness:-

$$Net\ flux = Primary\ Productivity\ Flux + Gross\ Flux \qquad 4.i$$

Average values of the gross fluxes over the measurement period are shown in Figure 4.4.

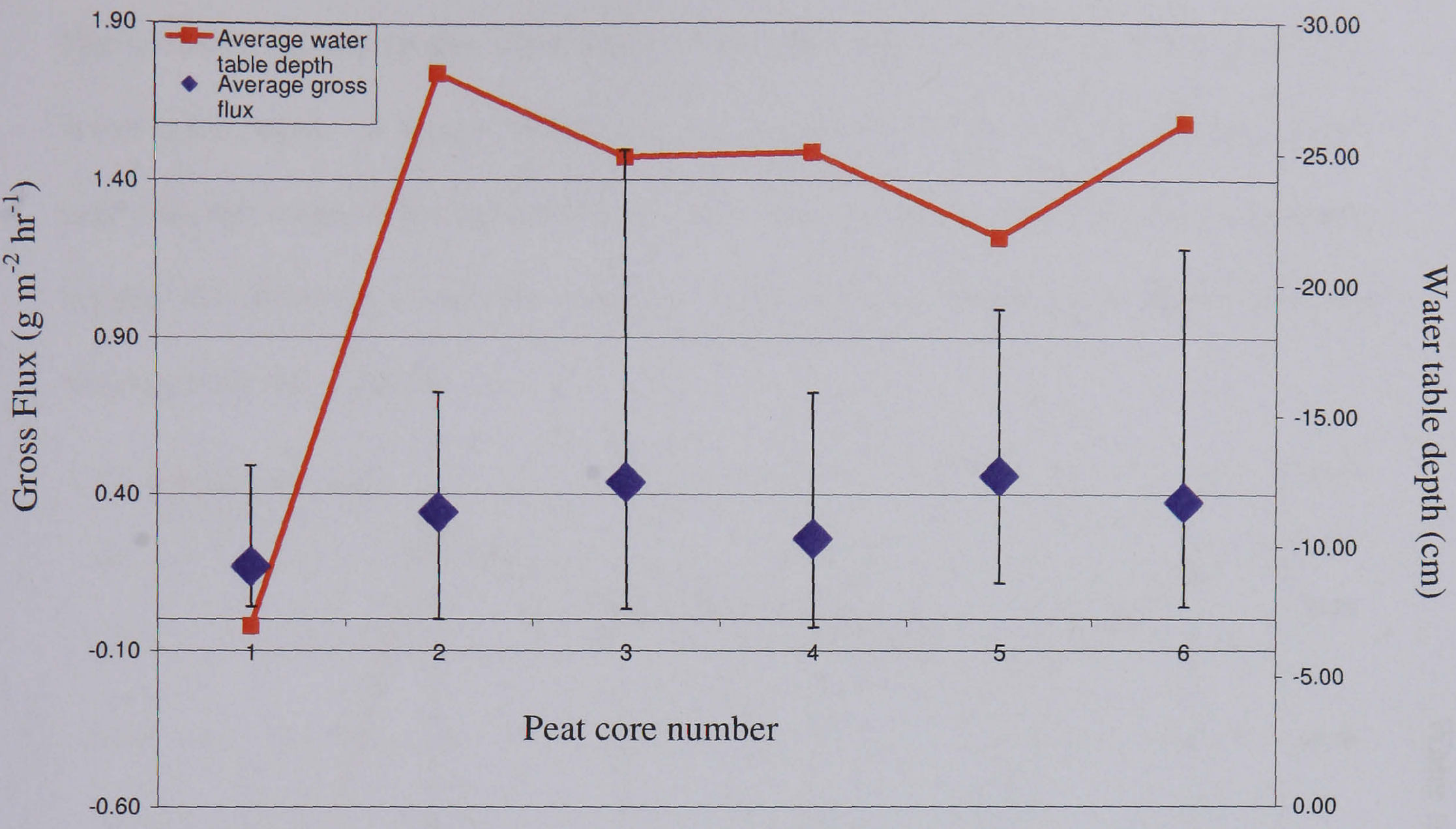

Figure 4.4 Average gross flux over sample period

As can be seen from Figure 4.4 the fluxes change with respect to the core number. The largest difference from the average flux was from cores 1 and 4. Core 1 has a below average gross flux and water table depth as this core was discarded after two weeks of measurements to be used in another project. Core 5 had the largest average release of carbon at 0.461 g CO_2 $m^{-2}h^{-1}$, and the lowest release of carbon (excluding core 1) was core 4 with a release of 0.259 g CO_2 $m^{-2}h^{-1}$. As can be seen by an overlay of water table depth all the cores (apart from core 1) have a very similar average water depth. This is to be expect as the water table depths was closely controlled for the first part of the experiment, and in the second part of the experiment the water table depths were kept at similar levels. Visually there is no clear relationship to the average water table depth and the average gross CO_2 flux.

The second relationship that there may be is a relationship between the net CO_2 flux and water table depth. A deeper water table is thought to simulate aerobic soil respiration, and a deeper water table depth will also allow roots to respire freely without being water logged therefore there may be a relationship between average water table depth and averaged net flux values:-

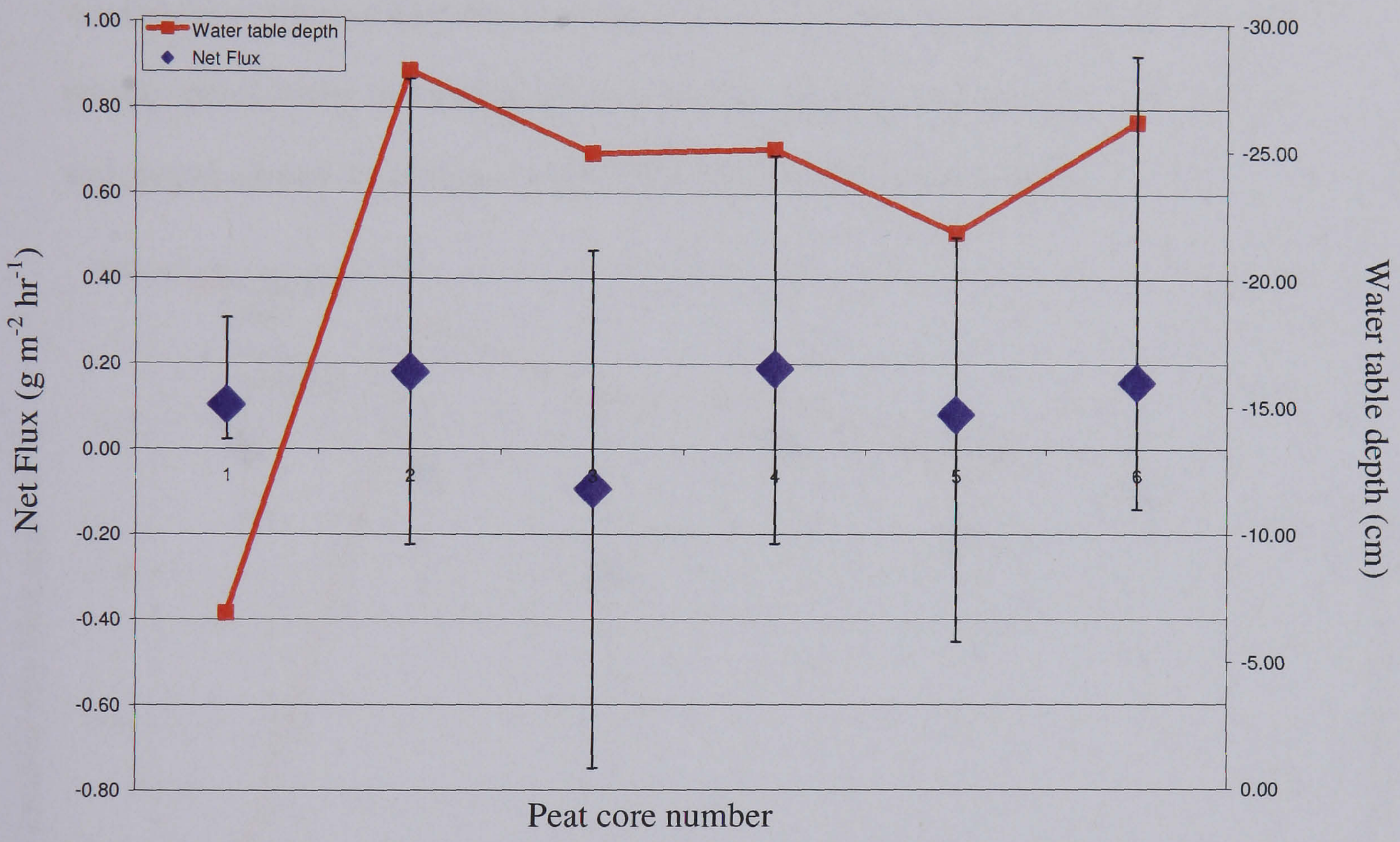

Figure 4.5 Average net fluxes over sample period

As can be seen from Figure 4.5 the net fluxes are much reduced compared to the gross fluxes Figure 4.4. The only core that is a net sink of CO_2 is core 3 which took up on average 0.09 g CO_2 $m^{-2}h^{-1}$. All the other cores are a net source of CO_2. This statement is not entirely accurate as the fluxes have only been measured over a three month period and are not a representation of the complete seasonal or diurnal cycles. The core with the

greatest release of average net CO_2 is core 4 with an average release of 0.189 g CO_2 $m^{-2}h^{-1}$. The average water table depth is the same as the average gross fluxes, and again there is no relationship between the average water table depth and net fluxes.

Net CO_2 fluxes are a combination of primary productivity and respiration, even though this was a single reading with the IRGA. This combination of combined fluxes may be masking any relationship between primary productivity and water table depth. Therefore primary productivity was calculated from the flux readings and averaged over the period and plotted against the averaged water table depth for each core (Figure 4.6).

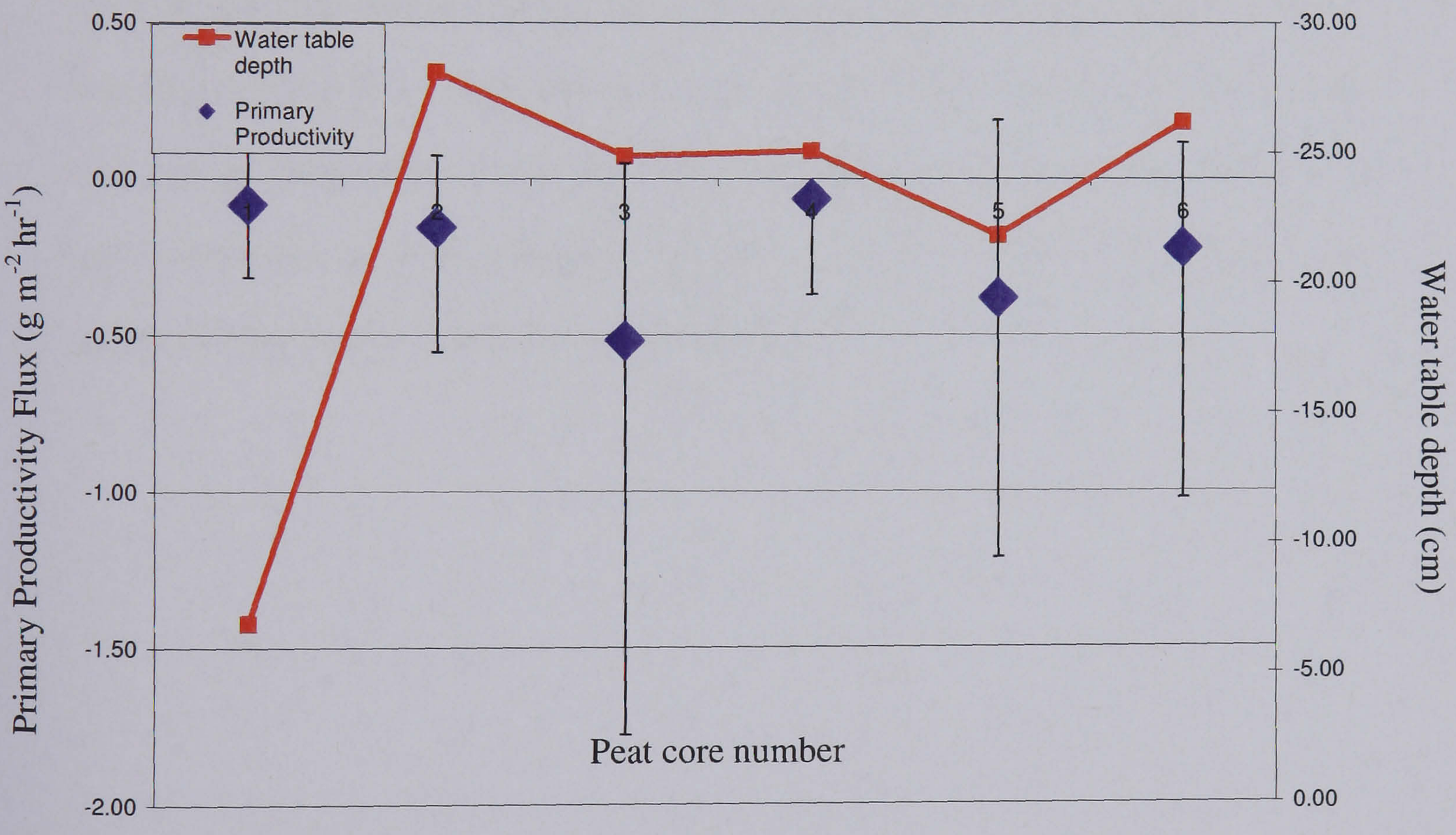

Figure 4.6 Averaged primary productivity fluxes over the sample period

As can be seen from Figure 4.6, core 3 has the largest average uptake of CO_2 of -0.520 g CO_2 $m^{-2}h^{-1}$. Core 4 has the smallest average uptake of CO_2 of 0.065 g CO_2 $m^{-2}h^{-1}$. The

water table depth again is the same as the two previous graphs. The first pattern to notice is that the cores that release the greatest amount of gross CO_2 are also the cores that take up the greatest amount of primary productivity carbon.

It is inappropriate to include a graph of gross, net and primary productivity fluxes over time because water table depth was increased weekly, and both PAR and air temperature changed daily, and because the measurements were taken over a three month period the results would not show a seasonal trend. A better graph would be to look at the relationship between driver variables (Air temperature, water table, and PAR) and flux. The first and most simple relationship is between soil temperature and gross flux as is described in Chapter 2. Although soil temperature was not measured, air temperature was, and soil temperature within the cores was thought to equal air temperature as the cores were unable to resist temperature changes in the air. A simple chart of gross flux against air temperature shows this relationship well:-

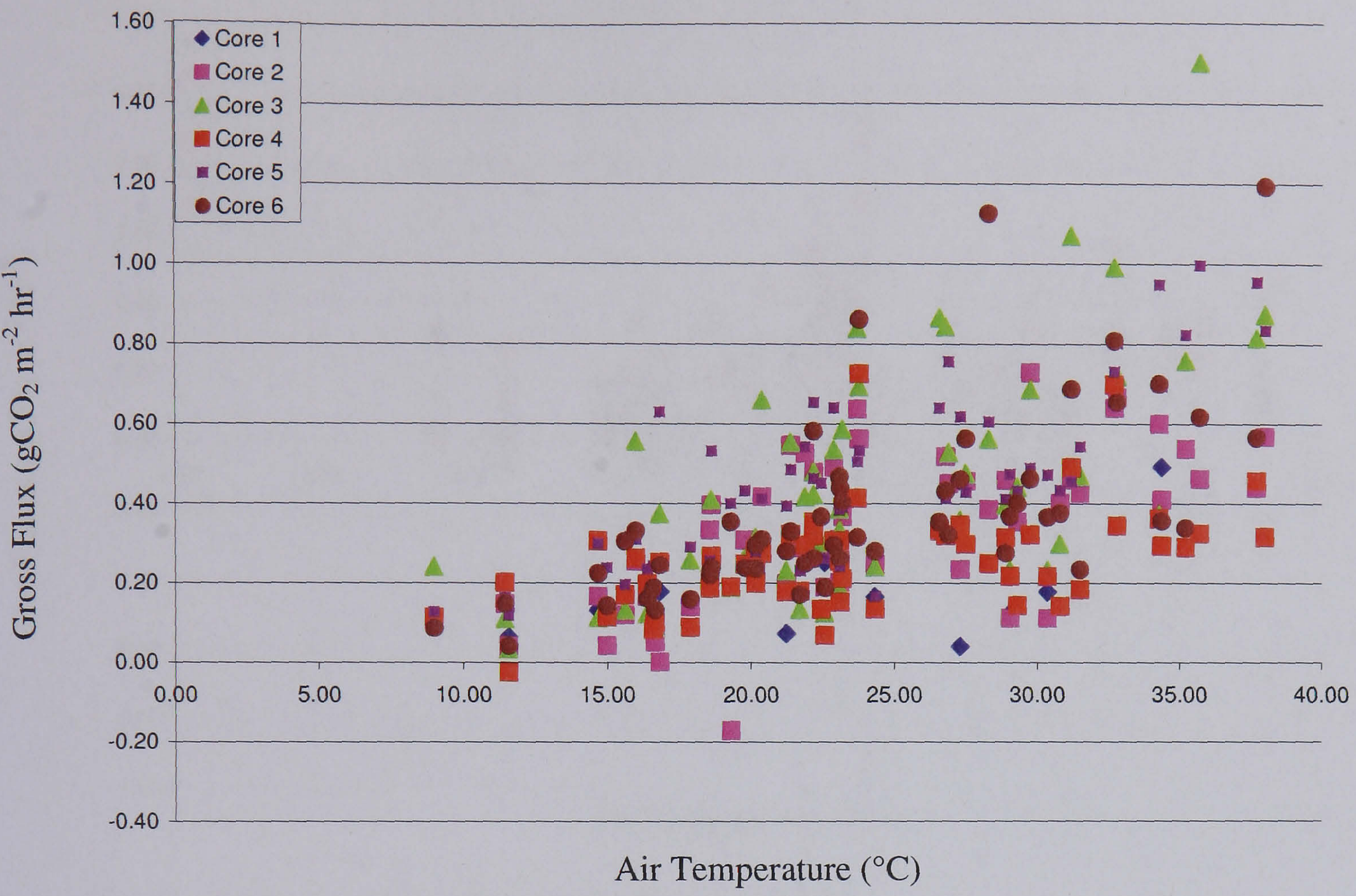

Figure 4.7 Gross flux against air temperature

As can be seen from Figure 4.7 the relationship could either be described as a linear relationship or a slightly non-linear relationship, however a relationship can clearly be seen. For just under 300 data points the relationship is fairly good, especially as changes in other potential driving variables, such as water table depth, have yet to be accounted for. To assess whether this relationship holds for net and primary productivity fluxes again a simple scatter graph should show this relationship (Figure 4.8).

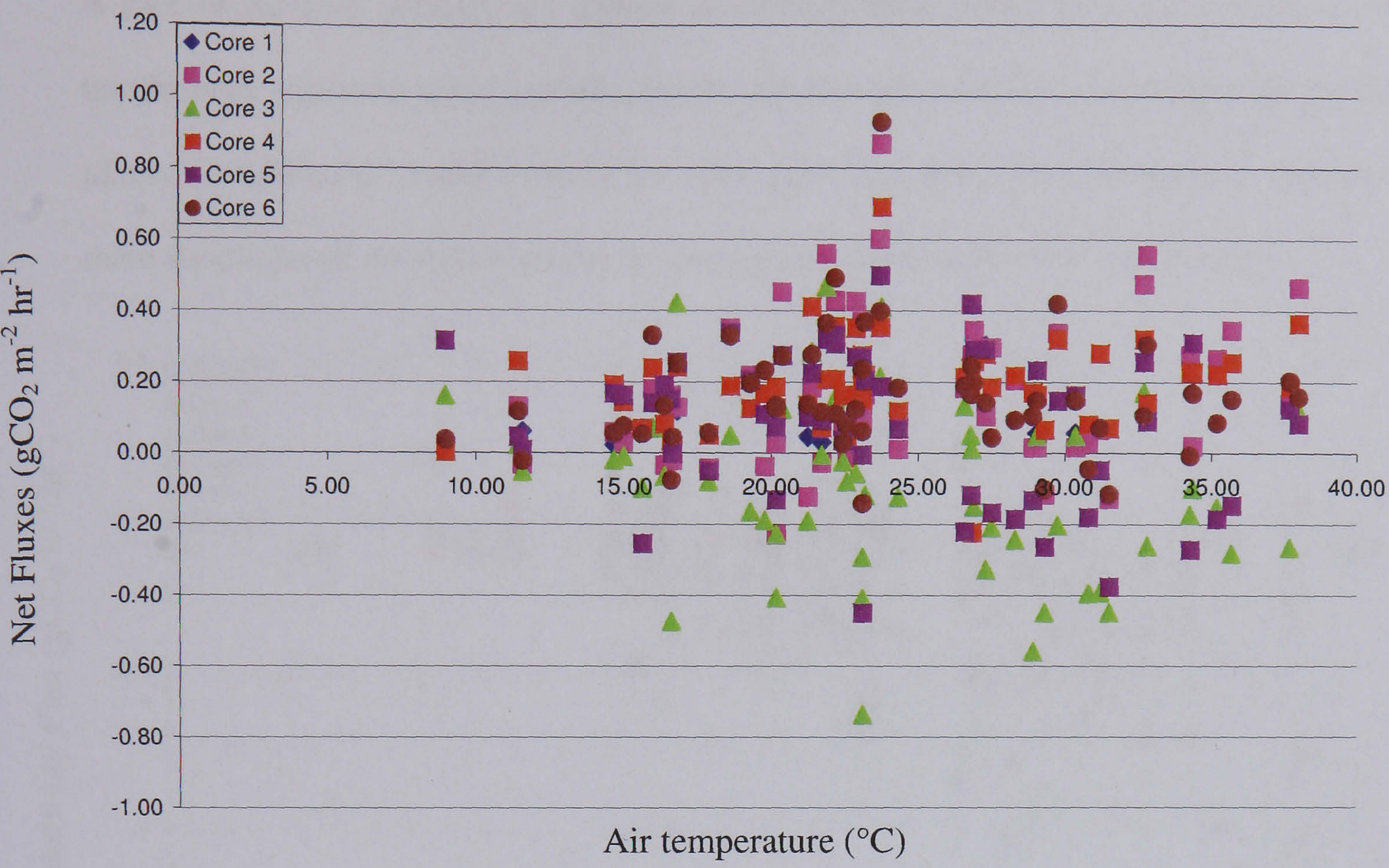

Figure 4.8 Net fluxes against air temperature

As can be seen from Figure 4.8 there is no direct linear relationship between net fluxes and air temperature, there is a spread of data around 23°C. The reason for this spread is that 23°C is approximately the median air temperature for the sample period, and the spread represents the amount of cloud level. For example, a day can be warm and cloudy, with little primary productivity, but soil respiration will still be high, and will plot as having a large positive number on the above graph (Figure 4.8). Alternatively, a sunny day will have a large primary productivity value, and the soil respiration will still be the same, so this will plot as a negative value on the above graph (Figure 4.8). The more results that are taken at a specific temperature with variable PAR and water table depth values would show the full range of values expected.

A plot of primary productivity against air temperature should have the effects of air temperature removed and represent purely the amount of CO_2 being taken up by the plants, assuming air temperature is the only driver for gross CO_2 production, therefore there should be no relationship between primary productivity and air temperature:-

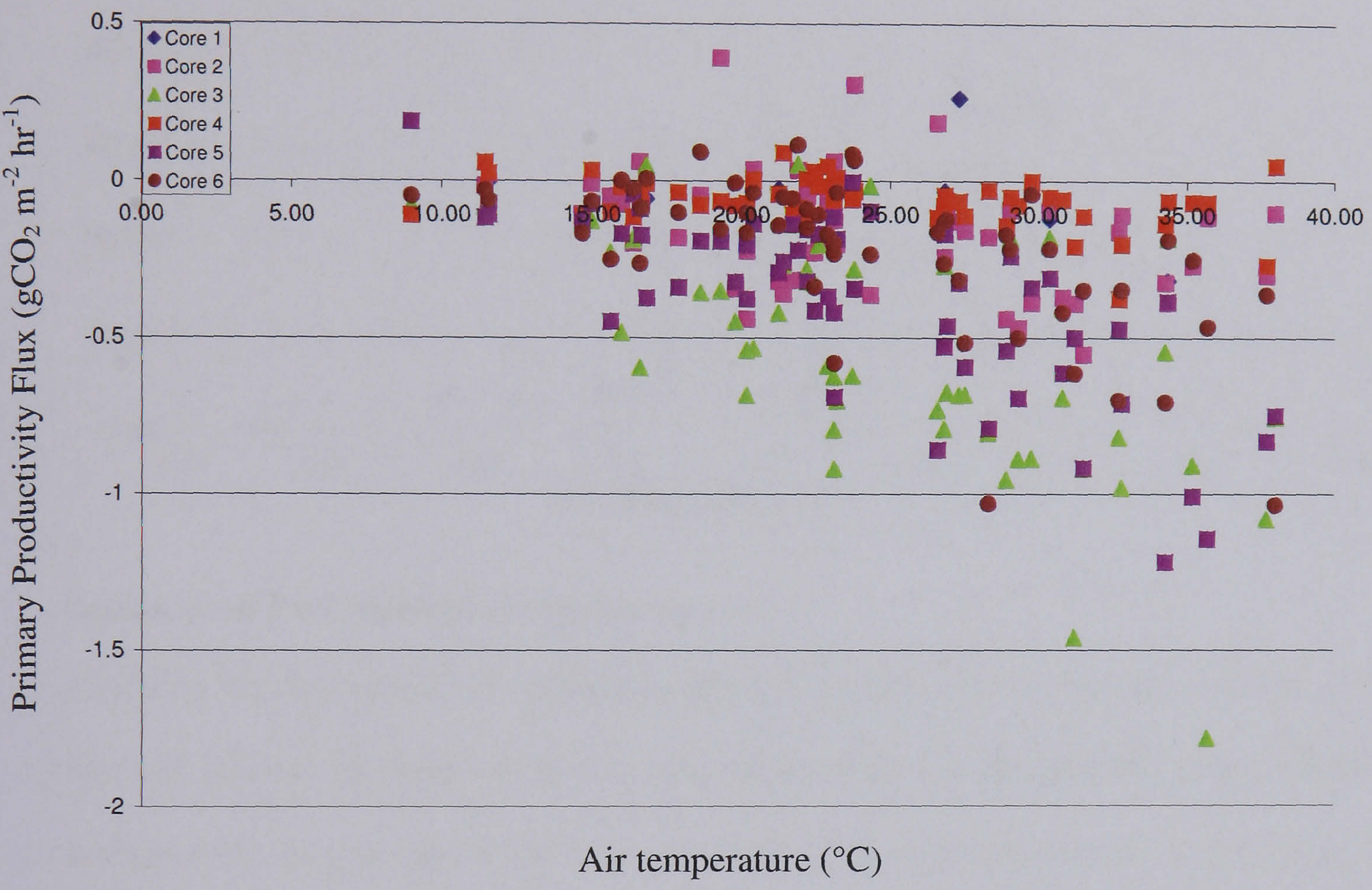

Figure 4.9 Primary Productivity Flux against air temperature

As can be seen from Figure 4.9 there is a pronounced inverse relationship between air temperature and primary productivity fluxes. The reason for this relationship is that normally when the temperatures are greater so are PAR levels, as sunlight will have a warming effect on the earths surface, and when temperatures are lower so are PAR levels, because when it is cloudy some of this heat from the sun will be reflected back into space so temperatures will be cooler. To prove this relationship between PAR and temperature a scatter graph clearly shows this relationship (Figure 4.10):-

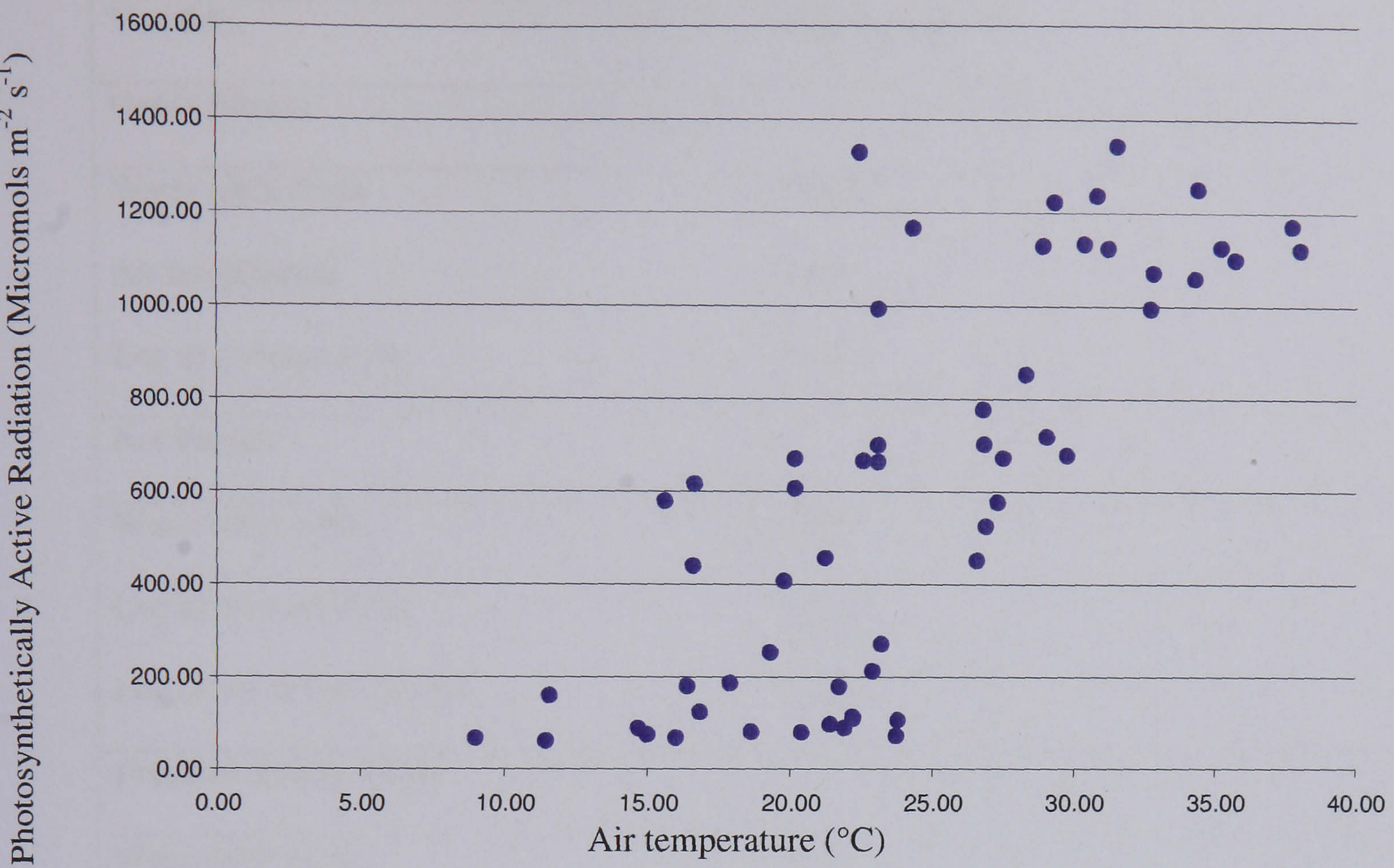

Figure 4.10 PAR against air temperature

Analysing the data statistically using multiple linear regression to analyses gross flux, net flux and primary productivity where; water table depth, air temperature, specific PAR, average PAR, Log average PAR, Log specific PAR, Log air temperature, and Log water table depth were variables. The difference between specific and average PAR is; specific PAR is the average PAR value for each individual CO_2 flux measurement, and average PAR is the average PAR value for all the CO_2 flux readings taken on that day.

Variable	Significance (P)
Gross Fluxes	
Water table depth	0.000
Air temperature	0.000
Log of average PAR	0.008
Net Fluxes	
Water table depth	0.000
Log of average PAR	0.006
Log of water table depth	0.000
Primary Productivity	
Water table depth	0.000
Log water table depth	0.000

Table 4.1 Multiple linear regression of variables against gross, net and primary productivity CO_2 fluxes

These results substantiate the view that air temperature only controls the gross flux - this is the conclusion found in Chapter 2. Therefore increases in average global temperature will have an effect on the gross CO_2 fluxes, increasing the overall gross CO_2 flux from the peat. Net and primary productivity fluxes were not significantly affected by temperature.

4.4.2. Effects of water table depth on CO_2 flux

The next relationship studied is the relationship between flux and water table depth.

Having looked at the averaged flux data in the previous section (Section 4.4.1) in relation to average water table depth (See Figure 4.4, Figure 4.5, and Figure 4.6) it can be said that there is no relationship between average water table depth and average CO_2 flux (gross, net and primary productivity).

From Table 4.1 it can be seen that there is a statistical relationship between water table depth and gross, net and primary productivity CO_2 fluxes. Therefore, the question remains; how does water table depth affect gross, net and primary productivity CO_2 fluxes?

The regression equations from Table 4.1 for the statistically significant terms are

$$Gross\ Flux = 0.0991 + 0.00374\ WTD + 0.0299\ AirTemp - 0.208\ LogAvgPAR \quad \textbf{4.ii}$$

$$Net\ Flux = 0.585 + 0.00558\ WTD - 0.183\ LogAvgPAR - 0.116\ LogWTD \quad \textbf{4.iii}$$

$$Primary\ Productivity\ Flux = 0.124 + 0.00391\ WTD - 0.191\ LogWTD \quad \textbf{4.iv}$$

From the regression equation (equation 4.ii) for gross flux it can be seen that the relationship between gross flux and water table depth is a positive relationship. This means that the greater the depth to water table the greater the amount of CO_2 will flux from the peat core surface. This is to be expected as it is hypothesised that the deeper the water table depth the greater the aerobic volume thus the greater the amount of CO_2 produced, and flux from the peat surface.

Net flux has a positive relationship with water table depth. As net flux is the sum of primary productivity and respiration net flux can either be positive (releasing CO_2) or

negative (taking up CO_2) depending upon soil temperature and PAR levels. From equation 4.iii a positive relationship would mean that as water table depth increased then net CO_2 would be come more positive i.e. it would release more CO_2 so this would mean that if the peat was taking up CO_2 then it would either take up less CO_2 or start to release CO_2.

Primary productivity also has a positive relationship with water table depth. Therefore the deeper the water table depth the more positive, or in this case less negative, the CO_2 flux would be. In chapter 2, it has been modelled that PAR is the only predictor of primary productivity. This regression analysis has shown that primary productivity is affect by water table depth. This implies that plant production is affected by water table depth. A reason for this could be that the plants are actually being affected by soil moisture, and as water table depth increases soil moisture decreases until the plants reach their wilt point, and to preserve moisture close some stomata's, reducing photosynthesis, thus reducing CO_2 uptake rate.

4.4.3. Effects of lowering or raising the water table on CO_2 fluxes

Having found a relationship between water table depth and CO_2 flux, the next test is the effects of raising or lowering the water table and the effect that has on the CO_2 fluxes. This statistically tested whether there was a difference between the CO_2 fluxes when the water table depth was increasing or decreasing. This analysis found that there was no difference in the fluxes whether the water table was increasing or decreasing at the 95%

confidence interval for gross, net and primary productivity fluxes.

4.4.4. Comparability of CO_2 flux results with CO_2 flux results from the Hexhamshire Common field site

Having found a relationship between the peat core CO_2 flux data and water table depth, and having found no relationship between water table depth and CO_2 flux at the Hexhamshire Common field site, (See Chapter 2) the results were analysed at to see if the two data sets (Hexhamshire Common data set and peat core data set) were comparable. If there is a relationship between the Hexhamshire Common field site CO_2 fluxes and water table depth that was being masked by other factors such as flushing CO_2 out of the peat at the Hexhamshire Common site, or CO_2 flux data was not measured over enough of a temperature range, and water table depths then a correction can be applied. A simple scatter graph of gross flux over temperature for both the data sets should show if the two sets are visually comparable (Figure 4.11):-

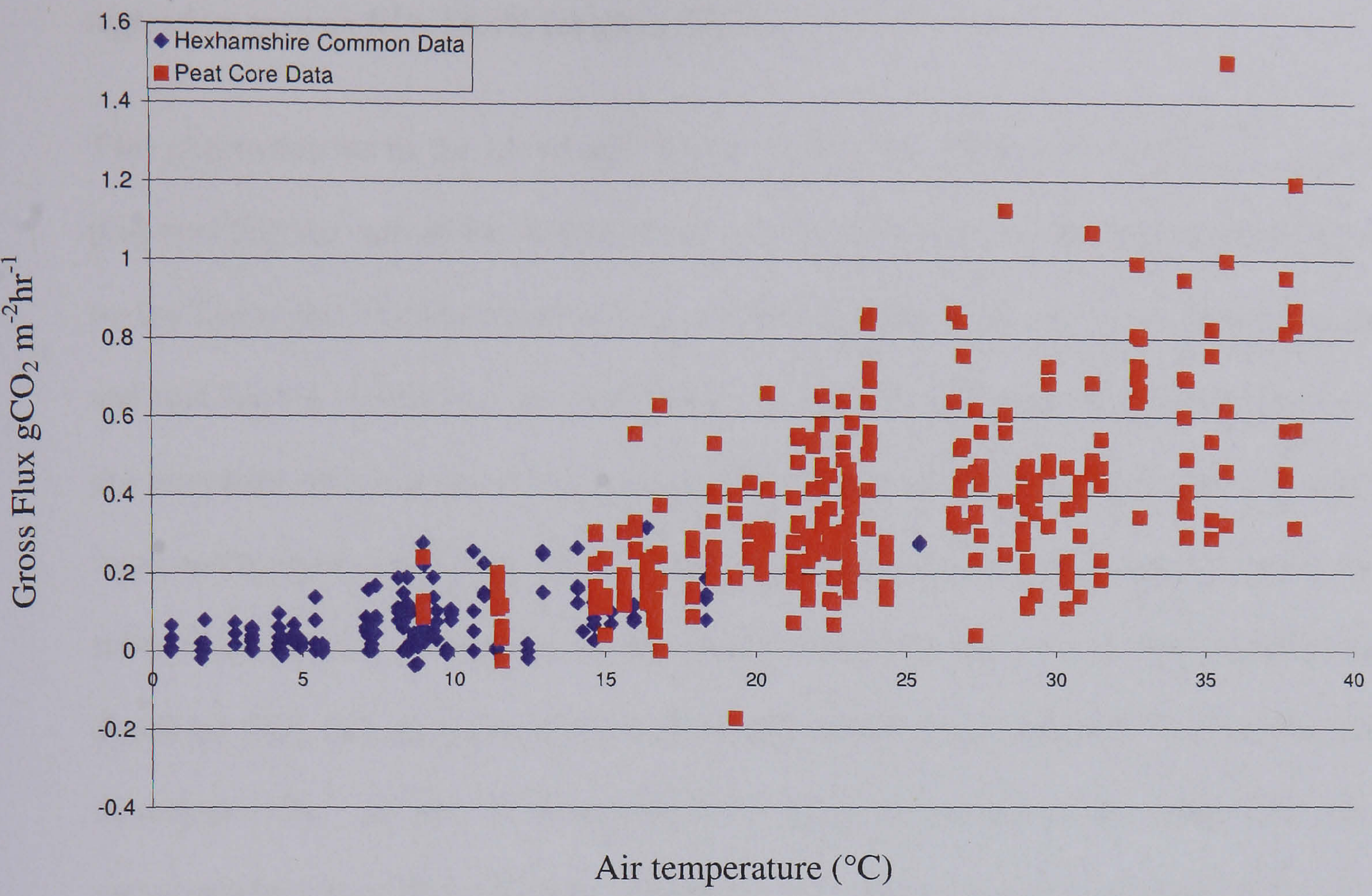

Figure 4.11 Hexhamshire Common field site gross flux data and peat core gross flux data plotted against air temperature

To prove a statistical relationship between the data sets, regressing the gross flux data against air temperature showed that air temperature accounted for 57.9% of the variance. The statistical test performed was to regress both data sets (Hexhamshire Common data and peat cores data) against the predicted values using the Lloyd and Taylor equation (Equation 4.v).

$$R = R_{10} e^{E_o\left(\left(\frac{1}{283.15-227.13}\right)-\left(\frac{1}{T_{soil}-227.13}\right)\right)} \qquad \textbf{4.v}$$

The R_{10} value for the data sets was a common value for all the data, and air temperature was used instead of soil temperature as in chapter 2 to ensure continuity between the two data sets as soil temperature was not measured in the peat cores. Multiple linear

regression gave an $R^2 = 58.4\%$ for gross fluxes.

Two improvements to the Lloyd and Taylor model were proposed in chapter 3. It was proposed that the sum of the dissolved and gaseous CO_2 fluxes could be predicted better, by the Lloyd and Taylor (equation 4.v), and that the R_{10} value was not a fixed constant and was linearly related to water table depth. In this cores experiment dissolved CO_2 was not measured however there was no lateral movement of water as the water movement was constrained by the UPVC tubes. There was a little vertical movement of water as the tubes were drained. Therefore it was though that there was no need to measure the dissolved CO_2 flux as most of the carbon lost would be by gaseous CO_2 release not dissolved CO_2. A plot of measured CO_2 flux, including the dissolved CO_2 flux measurements from Hexhamshire Common, was plotted against predicted CO_2 flux shows the relationship and the goodness of fit between the measured and predicted data. In this example the predicted data is excluding the relationship proposed in chapter 3, between water table depth and R_{10}, and shows that the sum of dissolved CO_2 flux and gaseous CO_2 can be better explain, using the Lloyd and Taylor equation by summing the two fluxes together (Figure 4.12).

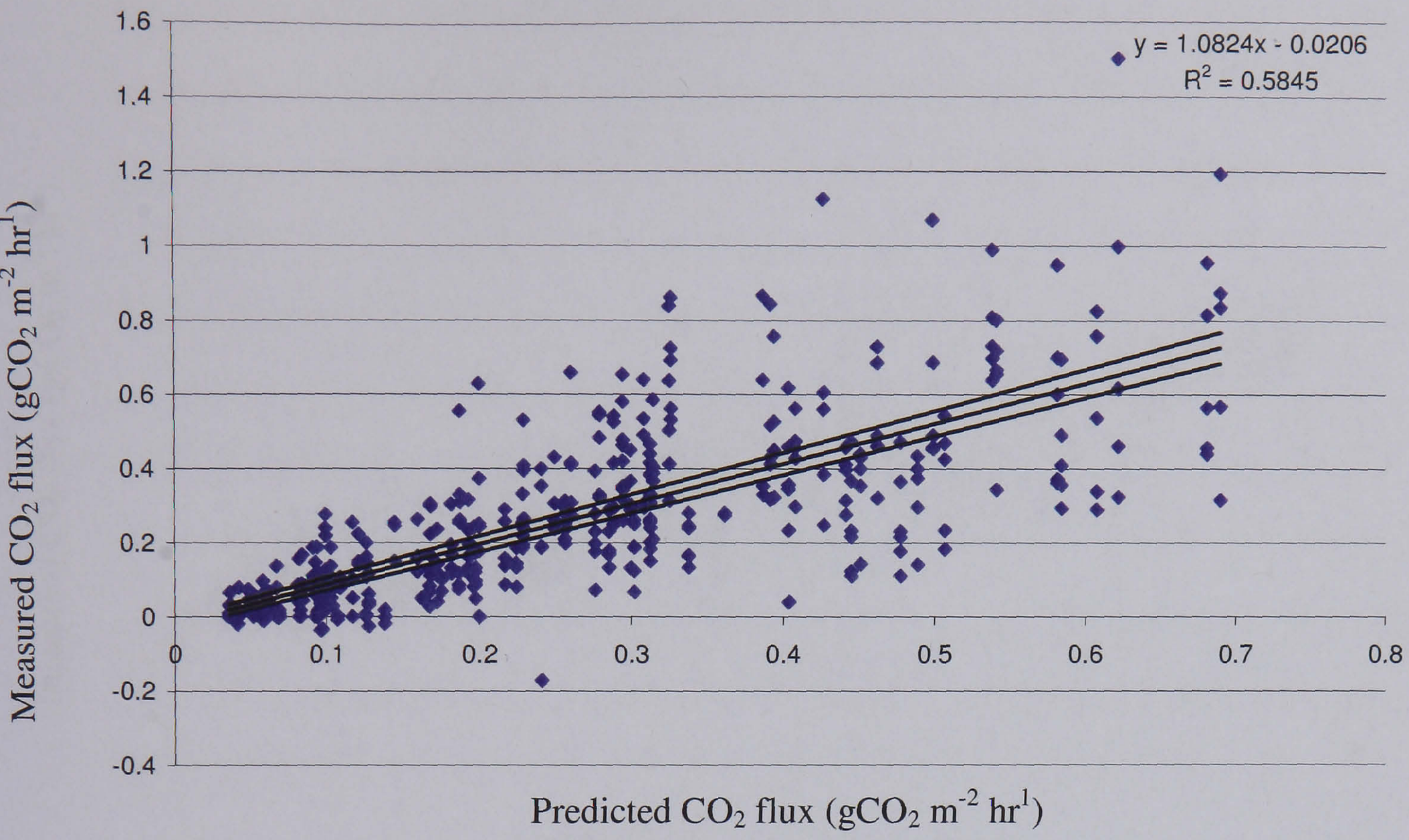

Figure 4.12 Measured CO_2 flux against predicted CO_2 flux with best fit, maximum and minimum error lines

As can be seen from the graph (Figure 4.12) there is a strong relationship between the measured data and the predicted data. This relationship is for all measured CO_2 flux from both the Hexhamshire Common field site and the peat cores, and has a common R_{10} value for all the data. As can be seen over 58% of the variance in the data can be explained by the Lloyd and Taylor equation. If the proposed relationship between water table depth and R_{10} is significant it should improved the amount of variance explained between the measured data and the predicted data. Therefore, a plot of measured CO_2 flux against predicted CO_2 flux incorporating the modified Lloyd and Taylor equation should have a greater R^2 value (Figure 4.13)

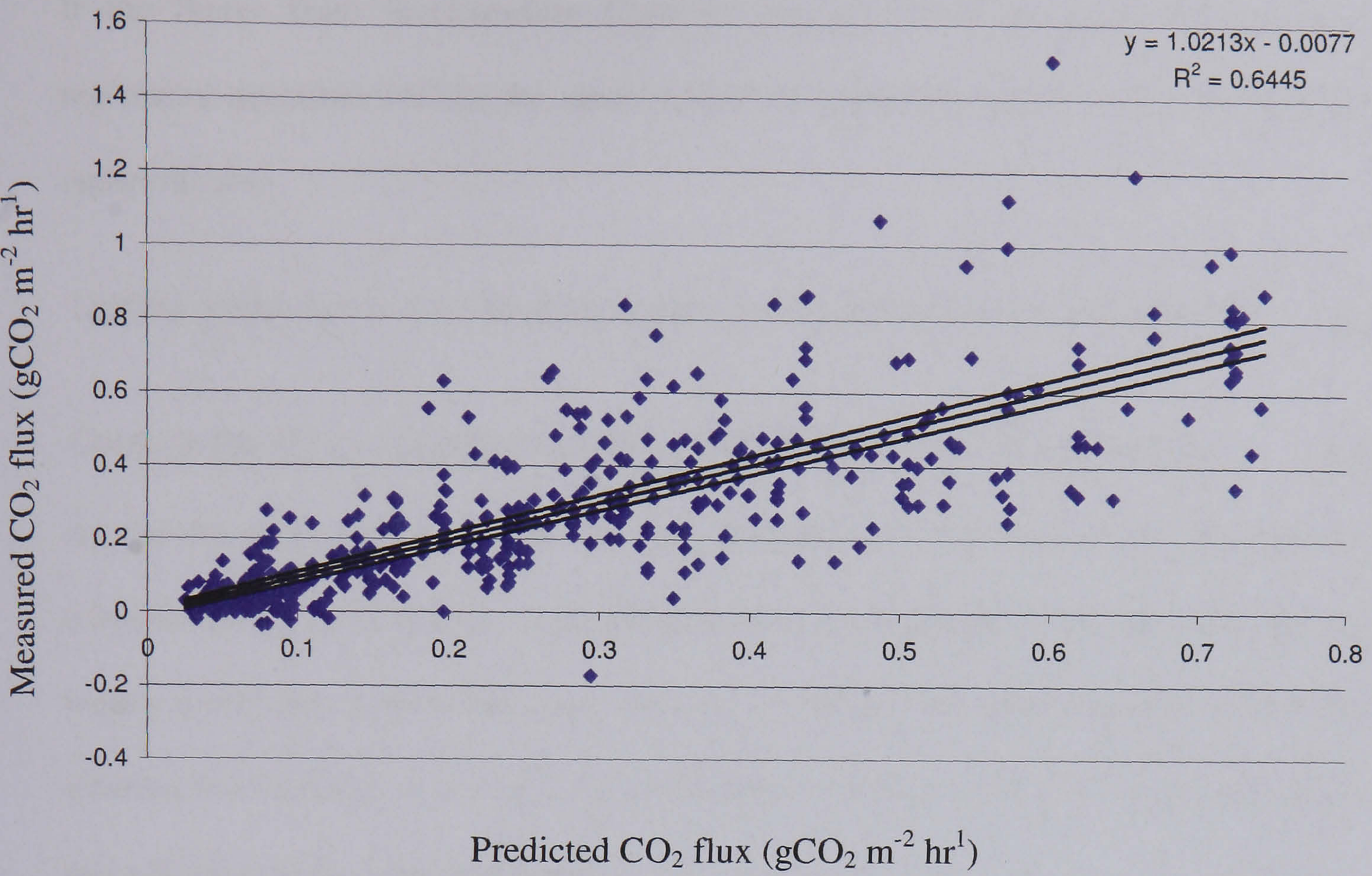

Figure 4.13 Measured CO_2 flux against predicted data using a modified Lloyd and Taylor equation with best fit maximum and minimum error lines

As can be seen from the graph (Figure 4.13), there is an improvement in the amount of variance predicted by this improved relationship between measured CO_2 data and predicted data.

Having used all the dissolved and gaseous data, for both the Hexhamshire Common data and the peat cores data as a continuous data set these data sets need to proved statistically, to be comparable. Plotting the flux data (both dissolved and gaseous) for Hexhamshire Common data against the predicted flux data for Hexhamshire Common and regressing the actual against the predicted using Minitab (ver. 14) gave the regression equation and the error of the equation. Regressing the flux data from the cores against the predicted flux data from the cores again gave the regression equation and the errors.

If the fluxes from Hexhamshire Common and the cores are comparable then the regression equations will be the same, within the errors calculated. The two regression equations are:-

$$\textit{Collars gross flux} = -0.014518(\pm 0.009441) + 1.0042(\pm 0.1034)\,\textit{Predicted flux} \qquad \textbf{4.vi}$$

$$\textit{Cores gross flux} = 0.0965(\pm 0.02362) + 0.94269(\pm 0.06127)\,\textit{Predicted flux} \qquad \textbf{4.vii}$$

As can be seen from equations 4.vi and 4.vii the intercept values are different even considering the error values. The gradient in these equations can said to be the same within error, thus concluding that the rate at which CO_2 was produced is the same whether from a collar or a core, however the initial amount of CO_2 produced at 0 degrees and a 0 water table depth is different.

To test whether the other fluxes (net CO_2 flux and primary productivity CO_2 flux) were significant, a plot of the two net flux data sets for the Hexhamshire Common net CO_2 flux data and the net CO_2 fluxes from the peat cores were plotted against PAR (Figure 4.14):-

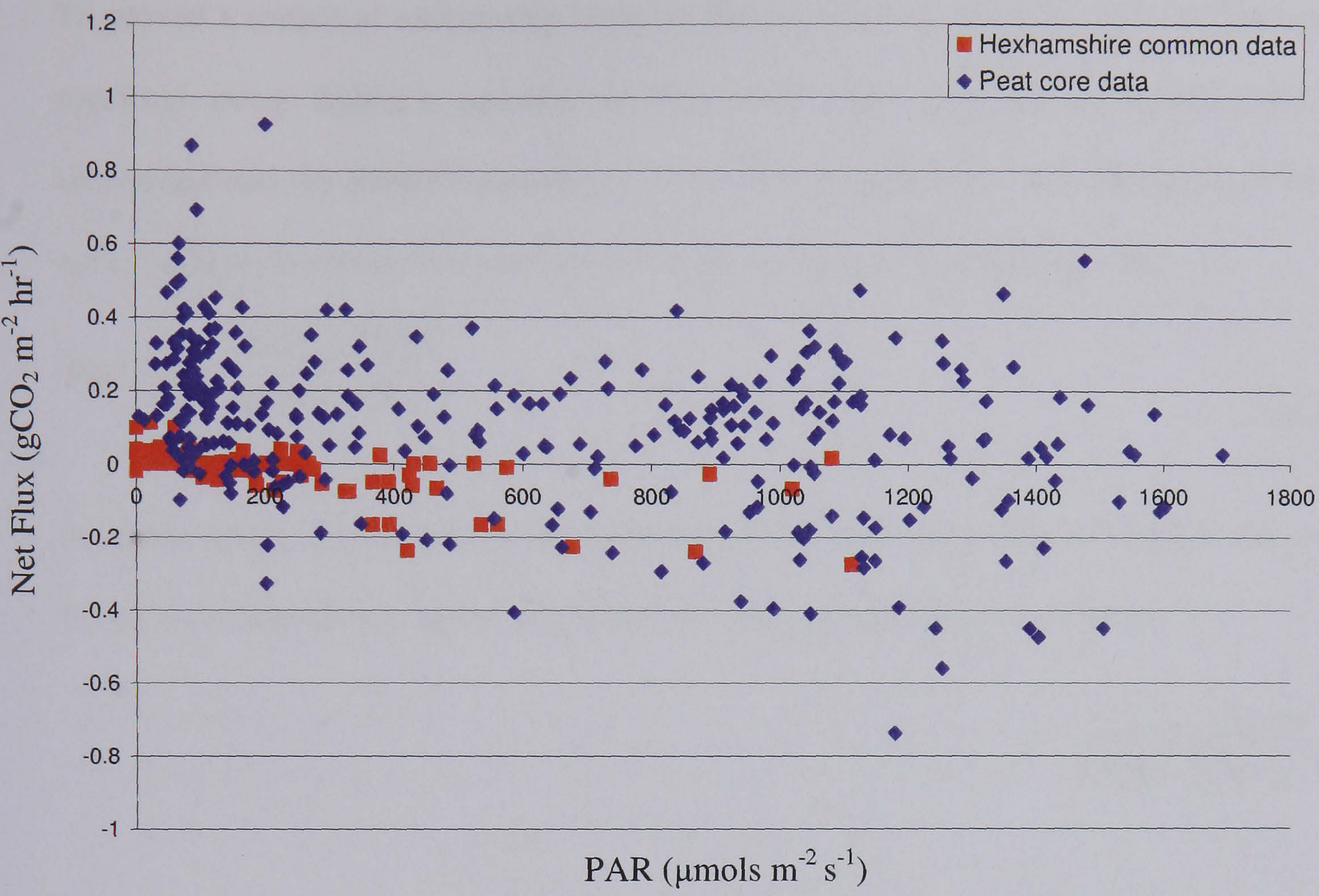

Figure 4.14 Net flux from Hexhamshire Common data set and net flux from peat cores

As can be seen from Figure 4.14, there is a visual correspondence between both sets of net data, with the data from the peat cores encompassing the range of the Hexhamshire Common variation. The data from the peat cores extends to a greater range of PAR readings and net CO_2 measurements. A reason for this could be that most of the peat core readings were taken in summer and at a higher average temperature, and fewer readings were taken in summer at Hexhamshire Common field site due to the land owners wishes. Another reason is that the peat cores were on average warmer than the collars at Hexhamshire Common field site, and net flux is a combination of gross fluxes and primary productivity fluxes (See equation 4.1) so on a warm day with low PAR the peat cores would, on average, release more CO_2 than the Hexhamshire Common collars.

To proved a statistical relationship between the two net CO_2 data sets, the net flux was predicted using Bubier's equation (4.viii) with Lloyd and Taylors equation (4.v) substituted into the Bubier equation (4.viii) to predict gross flux, and then the measured net CO_2 fluxes from the two data sets was regressed against the predicted data.

$$Net\ Flux = \frac{GP_{max}\alpha PAR}{\alpha PAR + GP_{max}} \qquad \textbf{4.viii}$$

A scatter graph of actual net data against predicted data should show whether the net fluxes are comparable from the Hexhamshire Common site and the peat cores

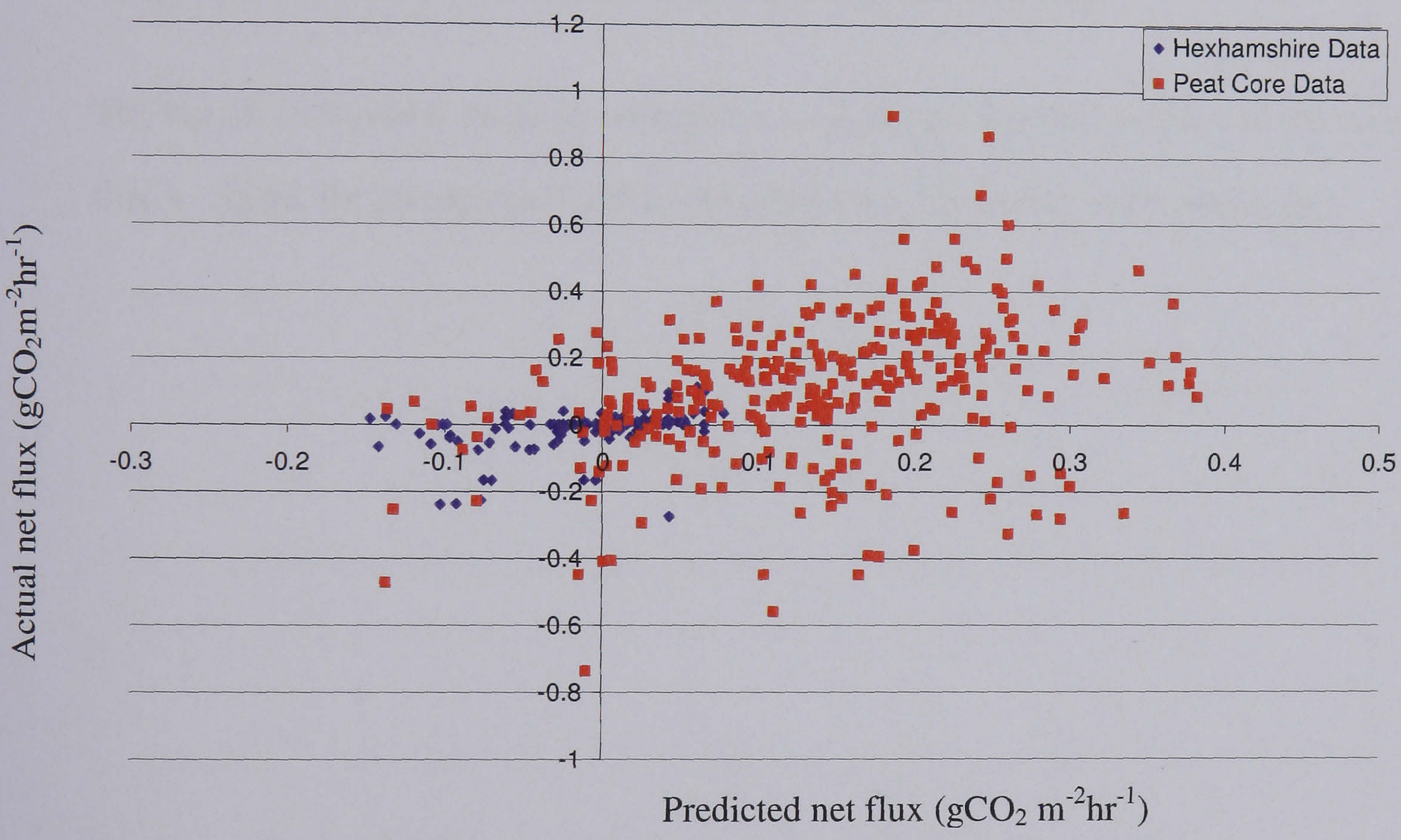

Figure 4.15 Actual net flux data against predicted net flux data

A regression of the actual data against the predicted data shows that 17.75% of the variance within the data has been explained. To test whether this relationship is significant, regressing the measured net CO_2 fluxes for Hexhamshire Common against the predicted fluxes will give a regression equation with errors this was repeated for the

core data to give another regression equation. Like the gross fluxes, these regression equations should be the same if the two flux data sets are comparable within error. The two regression equations are:-

$$\textit{Net Flux} = 0.020518(\pm 0.006221) + 0.13640(\pm 0.05593)\text{Pr}\textit{edicted flux} \qquad \textbf{4.ix}$$

$$\textit{Net Flux} = 0.00627(\pm 0.01865) + 0.60904(\pm 0.09133)\text{Pr}\textit{edicted flux} \qquad \textbf{4.x}$$

As can be seen from equations 4.ix and 4.x the intercept values are the same, within error, however the gradients, or rate of CO_2 production is different. So visually the data sets are comparable however when compared statistically they are different.

The last set of fluxes to study in comparison to predicted fluxes is primary productivity fluxes. Again, the primary productivity flux data from the cloches will be discarded.

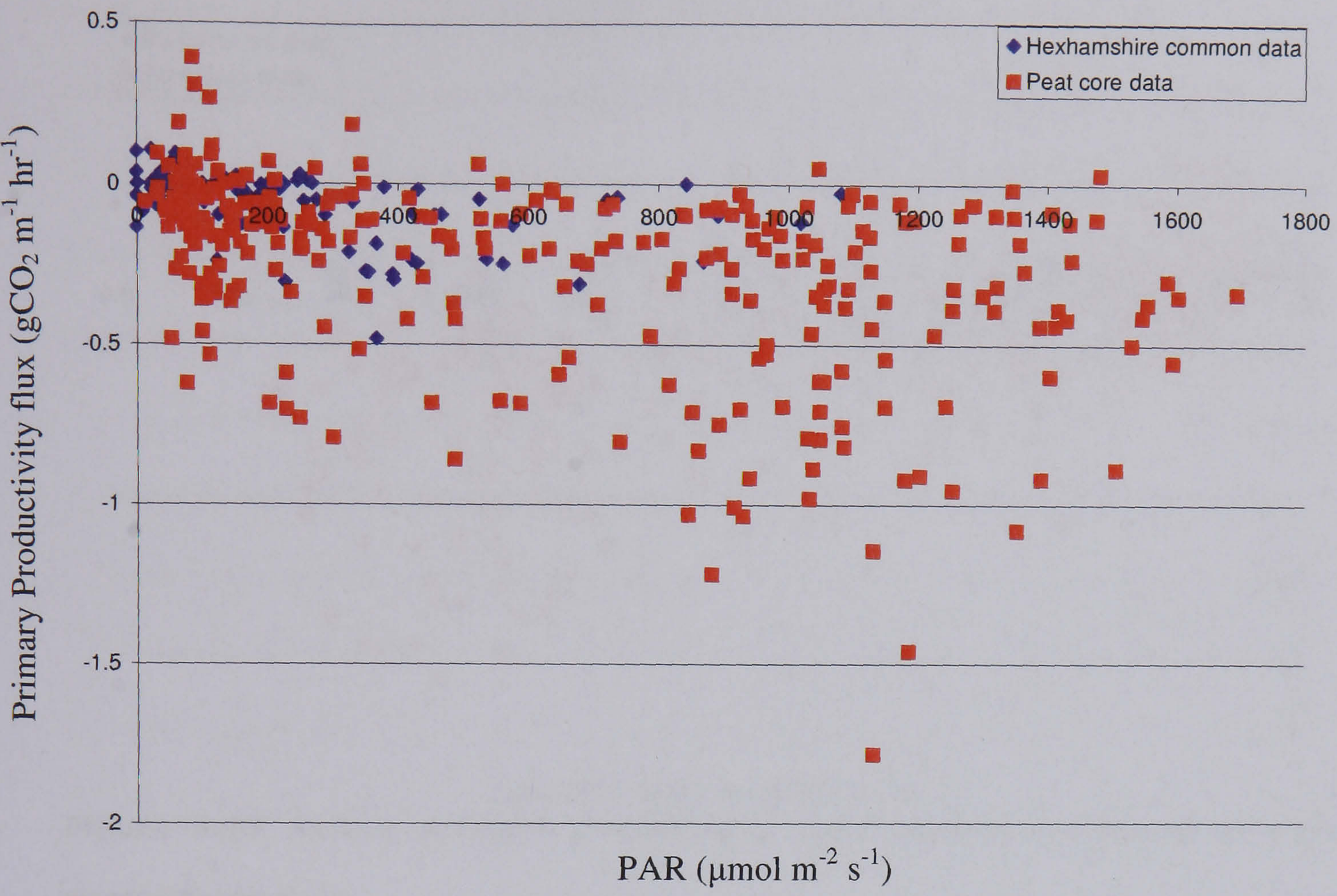

Figure 4.16 Hexhamshire Common primary productivity data and peat core primary productivity data plotted against PAR

As can be seen from Figure 4.16 the primary productivity data collected at Hexhamshire Common field site is comparable with the primary productivity data collect from the peat core data, again the data collected from the peat cores has a wider spread of values due to greater temperatures and higher PAR values.

To predict primary productivity fluxes the Bubier equation (4.vi) will be used without the Lloyd and Taylor equation to predict respiration, these predicted values will then be regressed against the measured primary productivity data to show if the data is comparable (Figure 4.17).

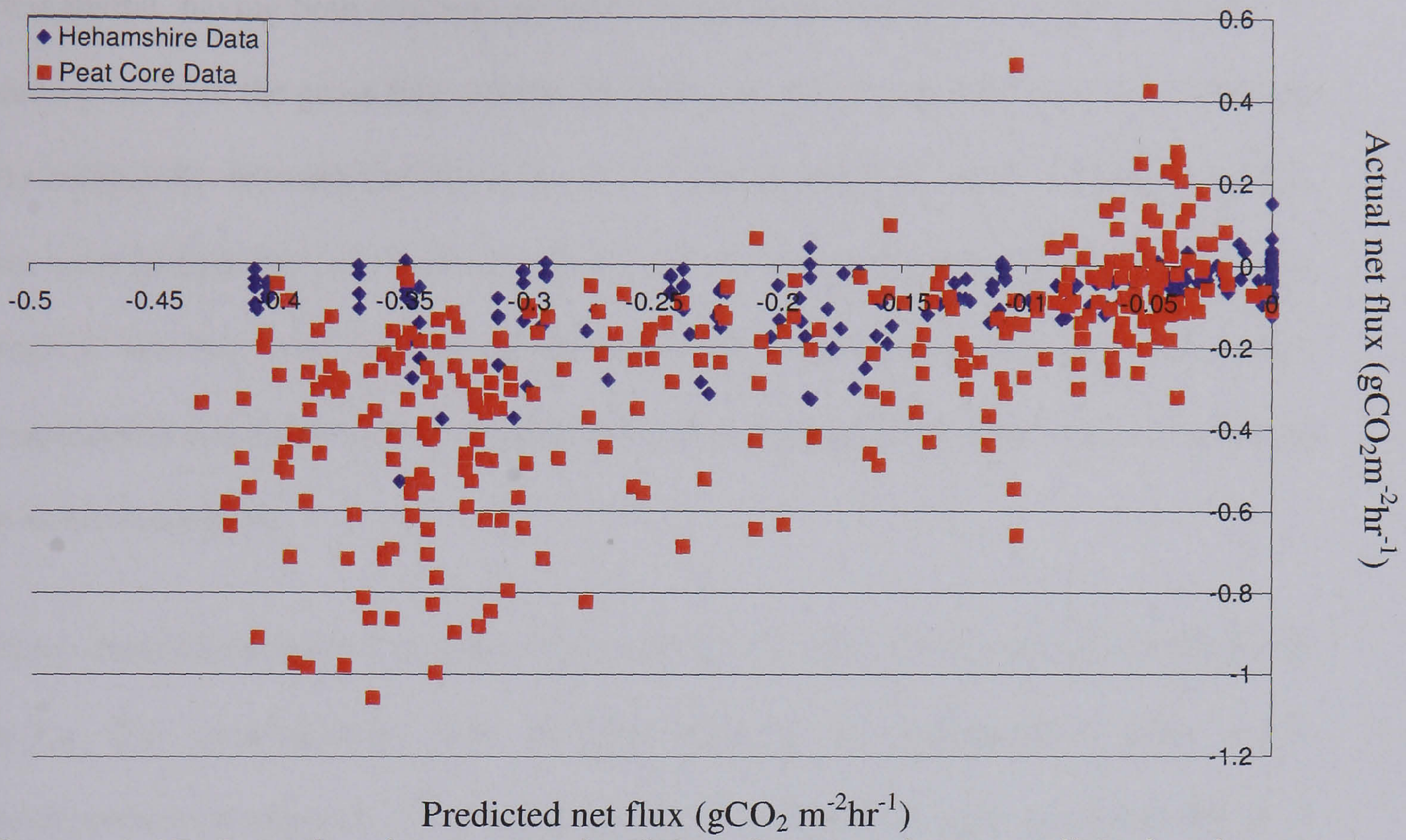

Figure 4.17 Actual primary productivity data against predicted primary productivity data

From the graph it can be seen that the data from Hexhamshire Common is comparable with the peat core data. To test whether these two primary productivity data sets are statistically comparable, regression analysis of the measured and predicted fluxes for both the Hexhamshire Common data and peat cores data was performed, and the regression equations for both data sets calculated with respective errors. If the two data sets are comparable these regression equations will be the same within error. The regression equations for the two data sets are as follows:-

$$PP\ Flux = -0.023733(\pm 0.009415) + 0.35882(\pm 0.05167)Predicted\ flux \quad \textbf{4.xi}$$

$$PP\ Flux = 0.05989(\pm 0.02364) + 1.5931(\pm 0.1066)Predicted\ flux \quad \textbf{4.xii}$$

As can be seen from these regression equations it can be said that the collars and cores

are different, having both different rates of CO_2 uptake and different intercept values. To summarise, from the gross flux regression equations, the rate at which CO_2 was produced was comparable between the two data sets, but not the intercept values. The two net data sets were comparable for intercept values, but not rate, suggesting the Bubier equation predicts net flux well at low temperatures and PAR values, but poorly at higher temperatures and PAR values. Finally, the primary productivity data sets can be said to be none comparable.

From observations made during measurements of CO_2 flux it was noticed that the initial, or C_0, CO_2 concentrations were different between the measurements made at the Hexhamshire Common field site and the peat cores. That is to say the initial measures of CO_2 ppm concentration made by the IRGA were 1) higher than the reported average 2002 atmospheric ppm concentration of 370 ppm (Hulme et al., 2002), and 2) the measurements of initial CO_2 concentration were higher from the measurements taken at Hexhamshire Common field site compare to the initial CO_2 concentrations made by the peat cores. The average initial CO_2 ppm value for Hexhamshire Common field site is 386.20 ppm and the average for all core data is 373.34 ppm. From these initial CO_2 values it would appear that the Hexhamshire Common measurements had higher initial CO_2 readings, even though the peat cores were measured at greater temperatures and water table depths. However, these values are not comparable because they are not corrected for altitude, as there is a density stratification of gas. Correction pressure due to altitude was according to the method of the Smithsonian Institute (1966) (Worrall *et al.*, 2005).

$$\frac{\textit{Atmospheric pressure at altitude}}{\textit{Atmospheric pressure at sea level}} = \frac{288\text{-}0.0065\textit{altitude}}{288}^{5.256} \qquad \textbf{4.xiii}$$

Further to this altitude correction, variation within the data also needs to be corrected for all of the climatic variables such as air temperature, water table depth and PAR. This was done using ANCOVA. The model response was the initial CO_2 measure, or C_0, and the model was defined as site and nested with site was collar number. The model covariates used were air temperature, PAR and water table depth. The results where then plotted on a main effects plot

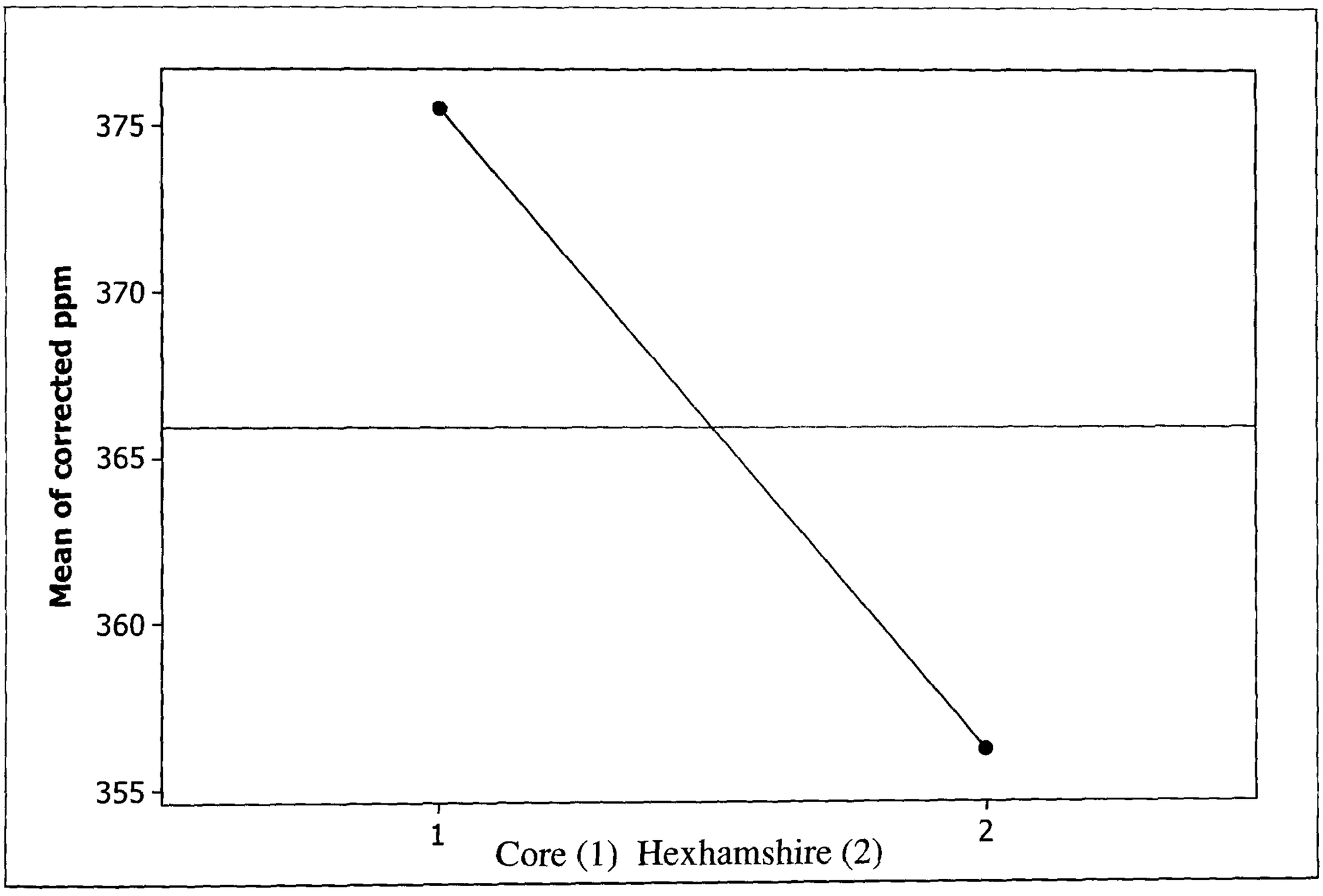

Figure 4.18 Main effects plot of initial CO_2 concentration from Hexhamshire Common and peat cores

As can be seen from the graph (Figure 4.18) there is a clear and statistically significant difference between the initial C_0 values for Hexhamshire Common and the peat cores.

However, it is not the results expected. The peat cores have a much higher initial CO_2 concentration than the collars at Hexhamshire Common. In fact the collars at Hexhamshire Common have an initial CO_2 concentration well below average ambient CO_2 levels, whilst the peat cores have CO_2 levels above average ambient CO_2 levels. Initially it was though that this difference could be explained by the fact that Hexhamshire Common is a net sink of carbon and therefore there would be a negative CO_2 diffusion gradient towards that peat with the CO_2 concentrations being very low in the boundary layer close to the peat. However, in the statistical analysis the amount of CO_2 taken up by the plants should have been accounted for by the variance of the PAR values, which have been shown, both in this study and in literature to be related to net CO_2 flux, but not to initial CO_2 concentrations. The regression equation for the relationship between air temperature, PAR and water table depth shows the relationship between these values and the initial CO_2 value

$$\textit{Initial } CO_2 \textit{ value} = 394 - 0.631\textit{air temp} - 0.00267\textit{PAR} - 0.189\textit{Water table depth} \quad \textbf{4.xiv}$$

From this significant (R^2= 30.8% n=950, P=0.000) regression equation, negative relationships between all of the variables can be seen. A negative relationship with air temperature would mean the higher the air temperature the lower the initial CO_2 concentration. This perhaps affects the pressure of the air causing a dilution effect that cannot be explained by a linear equation however including a log of air temperature in the regression equation does not improve the R^2 of the overall regression and changes the relationship between air temperature and initial CO_2 concentration from significant (P=0.000) to insignificant (air temp P=0.140, log air temp P=0.082). The same is true of

the logged values of the other variables in the regression analysis (Table 4.2).

No logged values	P	Logged values	P
Air temperature	0.000	Air temp	0.140
		Log air temp	0.082
PAR	0.002	PAR	0.235
		Log PAR	0.525
Water table depth	0.000	Water table depth	0.069
		Log water table depth	0.074

Table 4.2 Regression analysis between logged and none logged values for air temperature, PAR and water table depth

A negative relationship between PAR and initial CO_2 concentration values would also mean that the higher the PAR levels the lower the initial CO_2 values. Again this could possibly be explained by plants taking up CO_2 and again causing a negative CO_2 gradient between the atmosphere and the peat, however it is though that this is accounted for in the regression equation. From this, it is concluded that the change in initial CO_2 concentration is due to a variable that was not measured. It is proposed that this variable is water vapour. According to the ideal gas law, there are a specific number of molecules in a fixed volume of gas which changes according to pressure and temperature of the gas. In air, most of the molecules are comprised of Nitrogen, being the most abundant atmospheric gas, with the rest of the gas composed of the lesser gasses such as oxygen, CO_2, water vapour and other minor noble gasses. Each of these gases has a specific weight, and depending on the different compositions of gasses in the specific volume of air, the volume of air will have different densities. One molecule of Nitrogen in the

atmosphere has the atomic weight of 28 as it occurs in the N_2 form; oxygen is similar also occurring in a diatomic state, having a weight of 32. Water has a molecular weight of 18, which is lighter than the other gases comprising the major percentage of atmospheric gases. Therefore the greater the percentage of water vapour in a specific volume of gas the lower the density having a dilution effect on the other gasses in specific volume. The density of air can have the units of mg L^{-1}, this is equivalent to ppm therefore the greater the amount of water vapour in the atmosphere the lower the ppm concentration measured by the IRGA. This change in initial CO_2 values will not have an effect on the CO_2 flux because flux is the change of CO_2 concentration over space and time rather than being related to density.

So is this a reasonable assumption to assume that water vapour is causing this effective dilution of atmospheric CO_2? The inverse relationship with air temperature would mean that the greater the air temperature the greater the amount of evaporation, thus increasing ambient water vapour pressure. This would also be true with an inverse relationship with PAR. The greater the PAR levels the greater the amount of evapotranspiration from the plants, again increasing the amount of water vapour in the atmosphere. The inverse relationship between water table depth and initial CO_2 concentration is hard to explain, but it thought that water table depth is loosely related to air temperature where the greater the air temperature the deeper the water table depth. From eddy covariance, measurements the partial pressure of H_2O is also measured so that the concentration of CO_2 in the air sample can be corrected for water vapour density and latent and specific heat fluxes. Therefore, it is reasonable to assume that the difference in initial CO_2

measurements is a function of altitude and dilution by water vapour.

4.5. Discussion

It can be seen from the statistical analyses (Table 4.1) of the flux results (Gross, net, and primary productivity CO_2 fluxes) from the peat cores that the fluxes were linked to water table depth. This result is in contrast to the findings from the Hexhamshire Common field site where no significant relationship between the water table depth and any of the CO_2 fluxes was found. There could be several reasons for this:-

The first reason could be that the gas fluxes being measured from the Hexhamshire Common field site were not representative of the gases fluxing from the peat at the field site with respect to soil temperature, PAR and water tables depths.

The second is that the IRGA is measuring the total gas fluxes coming off the peat in the peat cores whereas for the field site only one of the pathways of CO_2 flux was measured by the collars at the Hexhamshire field site. This is because the CO_2 fluxing from the peat cores has only one route to the surface, and this is out the top of the peat core. On the field site the collars that were fitted permanently onto the peat were only ten centimetres in height, of which only five centimetres was below the surface. At this stage it is helpful to imagine CO_2 being produced in the peat as a point source. This point source of CO_2 could be being produced at any depth within the peat, and by the time it has reached the surface, by what ever process eg diffusion, ebullition, etc the concentration will not be the same as when it originated at the point source.

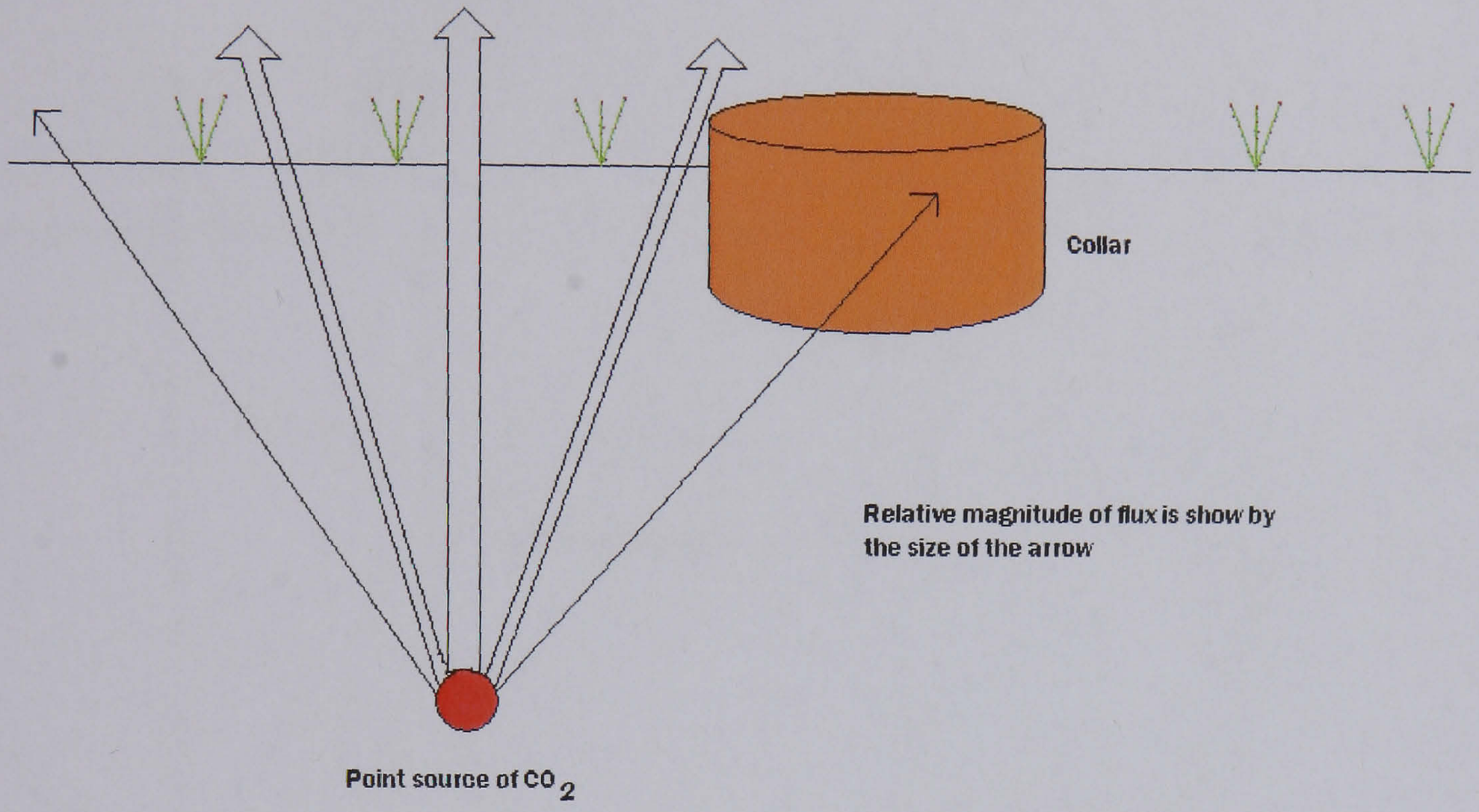

Figure 4.19 Point source of diffusion of CO_2 and relative magnitudes

Therefore the gas fluxes measured at the field site might not be representative of the CO_2 fluxes from the peat cores, however if enough measurements were made this error would average out and so is thought not to be important in this study. Another way to visualise the CO_2 fluxes from the field site is to imagine that CO_2 is only produced at the acrotelm / catotelm boundary, and that this surface is inhomogeneous due to overlying vegetation, geology, macropore flow, and surface drainage ditches. It can also be imagined that there is a continuous concentration of CO_2 produced at this water / soil boundary. If there are topographic highs and lows of CO_2 produced then this surface will act to concentrate some of the fluxes and spread out others. This again will lead to the variability within the flux measurements from the field site.

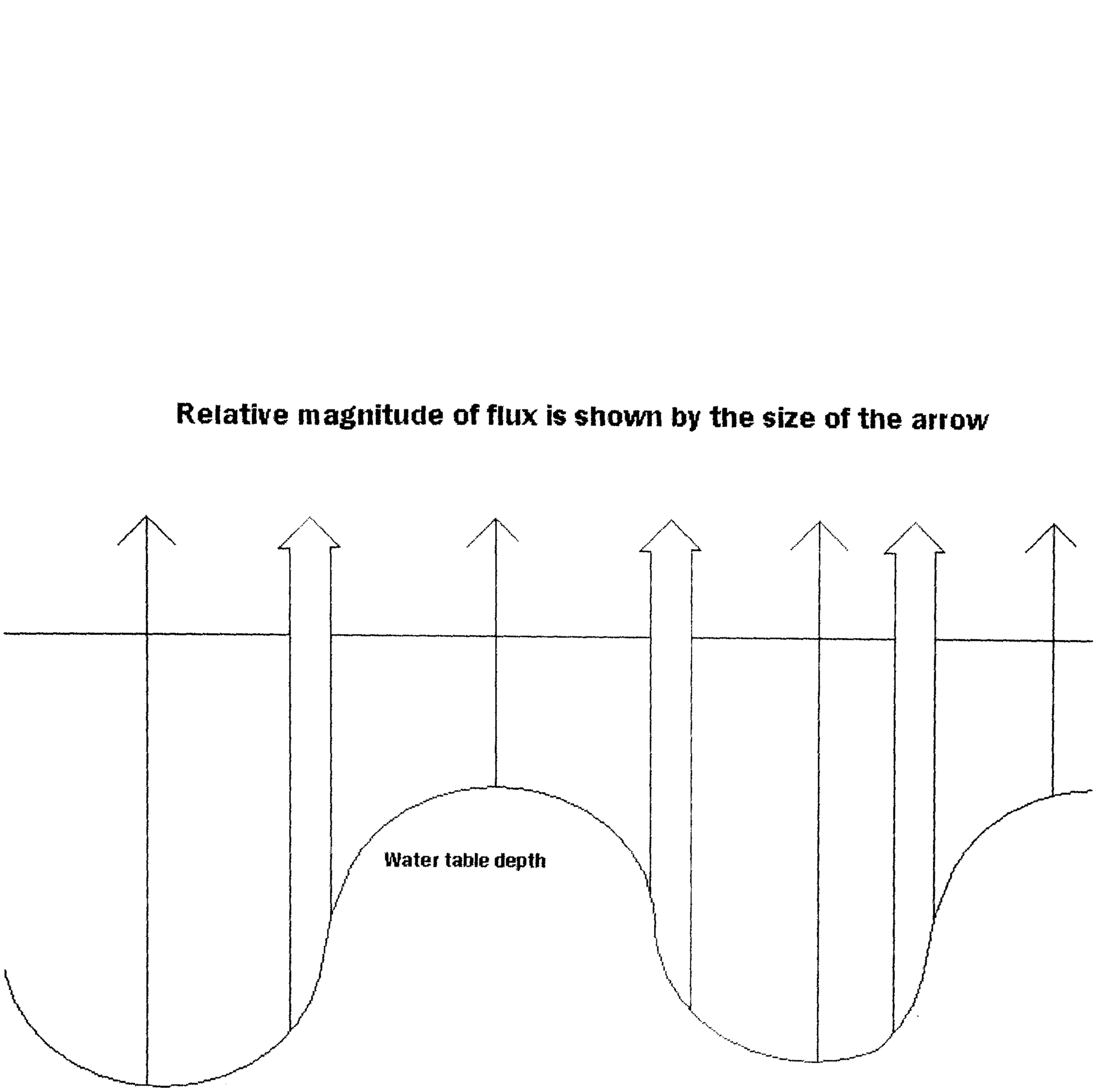

Figure 4.20 Water table depth concentrating CO_2 flux

Thirdly, there is no flow of water through the peat core as there is in normal peat and little of the dissolved CO_2 in the system is leaving the peat core as dissolved inorganic carbon (DIC).

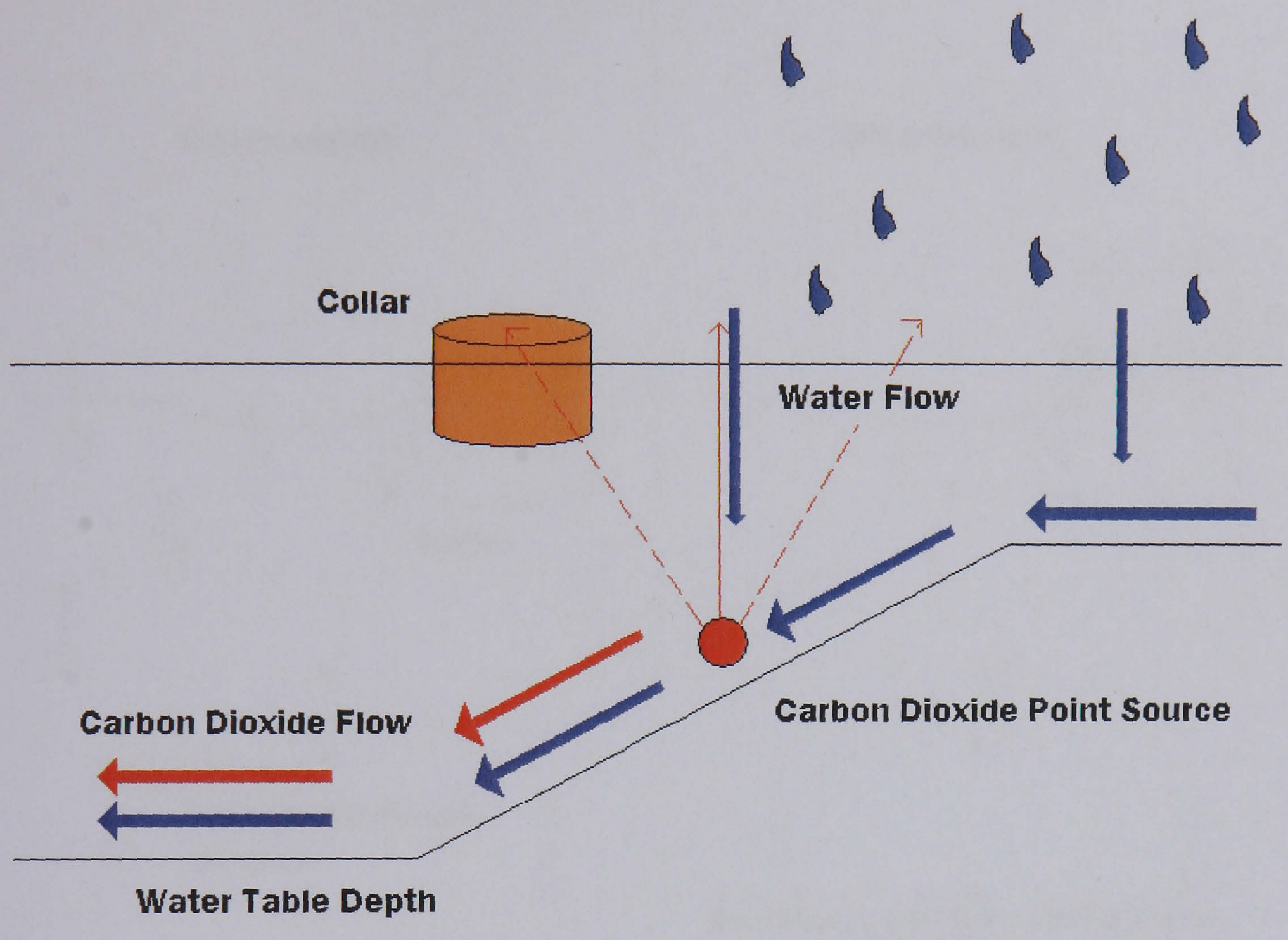

Figure 4.21 DIC flow

Fourthly, the peat cores are not being disturbed as much as the field site peat, there are examples in the literature (Nykänen *et al.*, 2003; Komulainen *et al.*, 1999; Alm *et al.*, 1999) that have stated that the simple act of walking across the peat will effect the gases being released from it.

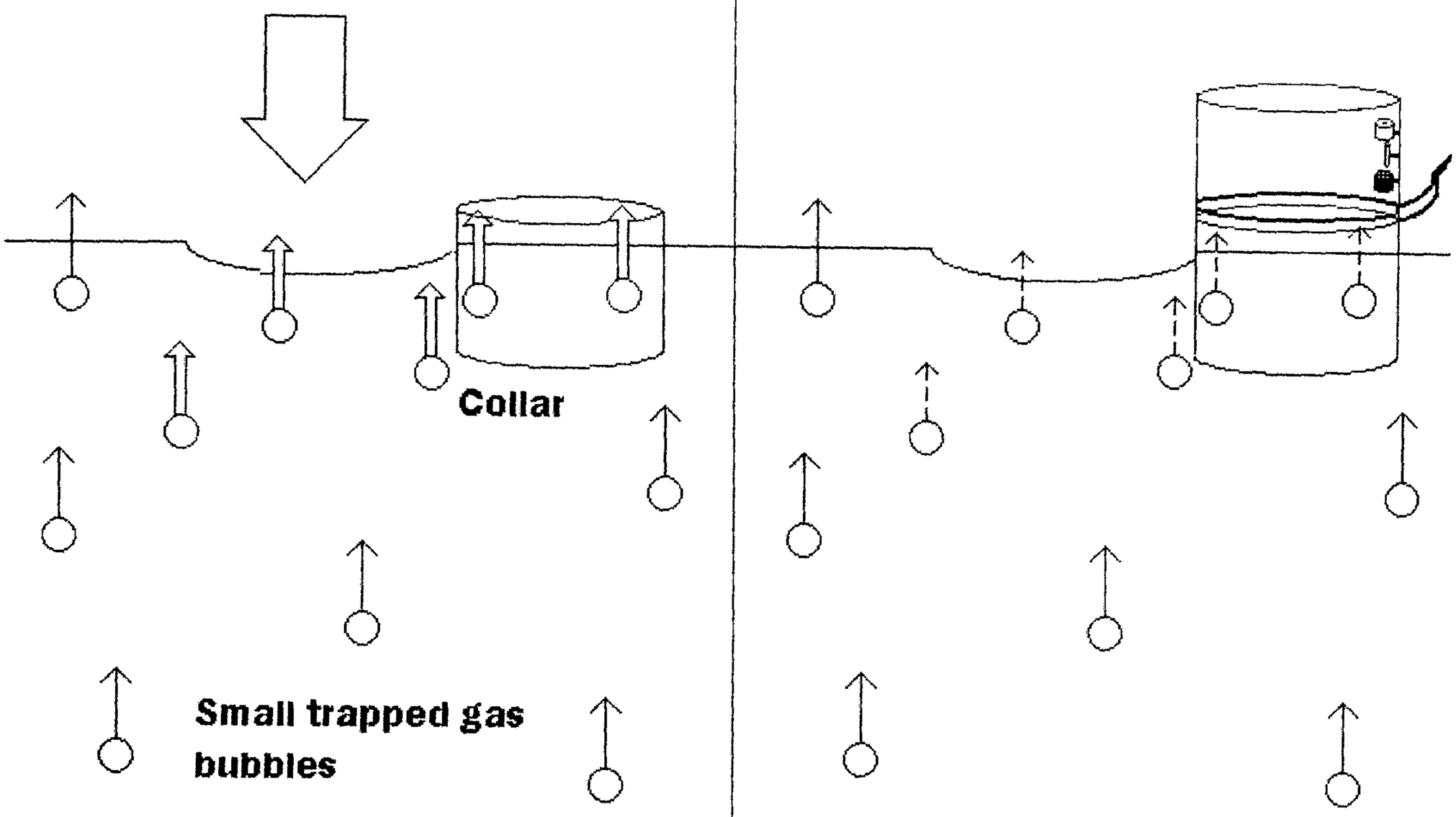

Figure 4.22 Walking across peat and releasing gas bubbles

Fifthly, the peat core were disturbed and compacted whilst they were being extracted, and this may have affected the fluxes from the peat cores.

Sixth, the peat core experiment was performed over a far greater range of water table depths and with a greater number of measurements both of these greatly increase the statistical power of the analysis and this give a far better chance of spotting any effect. After all the water table effect is secondary to the temperature effect.

Modelling the gross flux data showed that there is a good relationship between

temperature, water table depth in relation to gross flux. The implications of this are that fluxes measured here are independent of the fluxes measured at Hexhamshire Common which were used to model the relationship between water table depth and temperature. Therefore applying the equations used in to model the fluxes from chapter 2 and the improvements proposed in chapter 3 provides an independent validation for the relationships proposed.

From statistical analysis there was no difference between whether the water table depth was increasing or decreasing. This result is important as Freeman *et al.,* (2001) reported an enzyme latch mechanism which lead to greater concentrations of DOC when water table depth was restored pre-drought conditions. Therefore, it appears that gaseous CO_2 flux is linked only to water table depth and there is no interaction between water table depth and aerobic processes.

When the results were compared visually the flux measurements made from the cores encompassed the range of flux results measured at Hexhamshire Common. However, when the two data sets were analysed statistically it was found that only the gradient for the gross flux readings and the intercept values for net fluxes were comparable. Therefore, does this mean that the data sets were comparable or not? Using predicted flux data regressed against measured flux data only explained a maximum of 64% of the variance, and by the nature of the experiment the two data sets were measured over different temperatures and water table depths, with the peat core data set encompassing a greater temperature range than the flux measurements taken at Hexhamshire Common. If

a greater number of flux readings were taken at higher temperatures at Hexhamshire Common then this might help constrain the flux values to the values measured at the peat cores. It has also been noted that the Lloyd and Taylor equation is poorer at predicting fluxes at higher temperatures, so measuring fluxes from the peat cores at lower temperatures and shallower water table depths may help to constrain the regression equations between the peat cores and the Hexhamshire Common data sets. This statement is supported by the fact that in the regression equations the error associated with the constants is greater for the cores than the Hexhamshire Common fluxes.

4.5.1. Problems with the data

The most obvious problem with the data collected from the peat cores was the limited period of which flux measurements were performed. The fluxes were collected over a three month period and although readings were taken five times a week this will only give an indication of the fluxes over that time period. An improved understanding of the consequences of climate warming on the fluxes of CO_2 from peat would be achieved if a whole year of fluxes could be examined. A longer period of study would not only increase the range of temperatures at which the effect of changing water table could be measured but also examine seasonal effects which are not necessarily equivalent to temperature effects.

In drying the peat cores the peat would dry and move away from the walls of the core leading to the creation of a large aerobic volume of the peat with the ability to flux CO_2

to the surface more easily by being funnelled up the sides of the peat core providing a larger surface area in contact with the atmosphere, than if the surface was complete and unbroken. A complete and unbroken surface of peat would mean that CO_2 would have to diffuse through the peat, and the rate of diffusion would probably be slower than the effects of CO_2 being allowed to escape by funnelling up the sides of the core. An unbroken surface would also inhibit the influx of oxygen into the peat thus further reducing the rate of CO_2 production. Peat drying and moving away from the wall of the core would also allow oxygen to rapidly equilibrate with the interior of the peat core by increasing the surface area of the peat in contact with the air, ensuring that O_2 content was not a rate limiting step in the rate of CO_2 production.

4.6. Conclusions

In conclusion, it was found that an increase in temperature would only have an affect on the gross fluxes from the site. This was to be expected as this is the driver variable defined in the Lloyd and Taylor equation (Lloyd *et al.,* 1994). The other drivers affecting gross flux were water table depth, Log average PAR. Differences between cores are accounted for in the Lloyd and Taylor equation by the use of a core specific R_{10} value. Log of average PAR is a function of temperature as found in Chapter 2. Therefore, it can be said that an increase in average global temperatures will lead to a positive feedback with higher temperature, greater CO_2 flux, and with greater CO_2 flux more CO_2 in the atmosphere, which will increase average global temperatures.

Water table depth was found to be the only statistically significant term across all the data, affecting CO_2 fluxes for gross, net, and primary productivity fluxes. It was found that CO_2 was inversely related to water table depth, that is the greater the water table depth the greater the amount of CO_2 fluxing from the surface. This corresponds to results found in other literature that the greater the aerobic zone the greater the amount of CO_2 produced (Tenhunen *et al.*, 1995; Baldocchi; Hunt *et al.*, 2002; Wessolek *et al.*, 2002; Hashimoto *et al.*, 2006; Lloyd, 2006; Blodau *et al.*, 2004; Bubier *et al.*, 2003).

This experiment has shown that there is no increase in the amount of CO_2 released from the peat due to re-wetting the peat after a period of simulated drought. This correlates with the findings of Worrall *et al.*, (2006), who found that there was an enzyme latch mechanism linked to droughts, which increased the export of DOC by upland peat. It was found that this enzyme latch mechanism would not affect the aerobic production of CO_2 within the peat soils.

Field measurements of the CO_2 flux measurements taken at the Hexhamshire Common field site were visually comparable with the CO_2 flux results measured from the deep peat cores, but only a few terms were statistically significant from the regression equations, and none of the regression equations were completely comparable.

This is an important experiment and highlights the effect; that an increase in local temperature will increase the amount of gross CO_2 fluxing from the peat. It has also been shown that an increase in temperature will not increase the amount of CO_2 taken up by

the plants. This experiment also shows the effects that the drainage of peat lands will increase the CO_2 fluxes from the peat and the effect that draining peat already has had on CO_2 fluxes from upland peat, thus establishing a pattern between gross, net, and primary productivity CO_2 fluxes and water table depth.

A rise of soil temperature by 1^0C over a year will increase the soil respiration rate. Recalculating the overall carbon budget for the Hexhamshire Common site using the best estimate from chapter 3 reduces the amount of carbon taken up by the peat from 52.3 tC $km^{-2}a^{-1}$ to 39.1 tC $km^{-1}a^{-1}$, which is a reduction of over 13 tC km^{-1} a^{-1}. This is important because, a marginal peat that is still a small sink of carbon, a seeming small increase of 1°C could turn a peat from a sink of carbon to a source of carbon.

4.6.1. Further Experimentation

There are several further experiments that could be performed on this type of peat cores. The first are measurements of CH_4. This would provide a total gaseous carbon flux from the peat cores. This experiment would also provide information on the effects of increased temperature and lower water table depths on CH_4 production.

The second is to measure dissolved CO_2 concentrations from different depths within the peat, this would provide information on the mechanisms of dissolved CO_2 production such as if dissolved CO_2 is only produced at the catotelm / acrotelm boundary, or whether it is a stratified process, and what processes are important in the production of dissolved

CO_2. This information is important in monitoring the complete carbon losses from upland peat, and managing drainage schemes to reduce carbon losses.

The third experiment could be to spike the peat core with a stable isotope of carbon isotope (C^{13}), and take regular measurements of CO_2, CH_4, DIC and DOC (Dissolved Organic Carbon). This information would provide information on the turnover rates of carbon within peat and how stable the carbon reserves are at depth within peat cores. It would also provide information on how quickly plants can input carbon into the peat soil, and into what form, i.e. organic or inorganic carbon.

A fourth experiment could be to control atmospheric conditions and increase ambient CO_2 levels to simulate in increase in atmospheric CO_2 to provide information on whether peatland plants will take up more carbon when CO_2 concentrations were increased.

5. Chapter five: Calculation of Dissolved and Gaseous Carbon Budgets

5.1. Introduction

When measuring the carbon budget of any field site there are inherent problems which leave gaps in the data. When measuring gaseous carbon fluxes it is impossible to measure the fluxes from one area of land continuously even with an eddy covariance flux tower. The two main approaches for measuring gaseous CO_2 from a field site are; an eddy covariance method, and a closed chamber approach. The problem with an eddy covariance method is that the fluxes measured are limited to an area defined by wind speed, direction, turbulent air flow, and the complexity of a flux tower set up limits the measurements to a fixed location. Other factors affecting the measurement of eddy covariance fluxes include rain, which collects on the tips of the sonic anemometer, dispersing the sonic signal making CO_2 measurements impossible, and instrument failure, with typical down times in the order of 40-50%. The main problems with the closed chamber approach are: that fluxes cannot be measured continuously and extrapolations have to be made, the area that a closed chamber measures is also much smaller than a flux tower measures and may not be representative of the overall fluxes of the field site, this can normally be counteracted by multiple measurements. The advantage with a

closed chamber method is that the same area will always be measured, whereas a flux tower area varies with wind direction and speed. Measurement within a closed chamber can be made against a range of driving variables, including rainfall events, whereas a flux tower cannot measure during these periods. Therefore, a sensible approach is to calculate an overall carbon budget for a field site is to measure a representative area for flux values and scale these values up both spatially and temporally; this is normally done using a statistical approach. There are several different statistical approaches used to calculate a carbon budget, these are predominately based upon the sum of the measured carbon fluxes compared to different measured components such as soil temperature and PAR (Lloyd *et al.*, 1994; Bubier *et al.*, 2003). From an upland peat there are several different fluxes of carbon from dissolved CO_2, gaseous CO_2 released by the peat surface, to particulate organic carbon (Dawson *et al.*, 2004; Worrall *et al.*, 2003) to complete the carbon budget for a field site all fluxes need to be accounted for. The different types of carbon lost from an upland peat system can be summarised by a diagram by Worrall *et al.*, 2003, which shows the different pathways by which carbon can be lost (Figure 5.1).

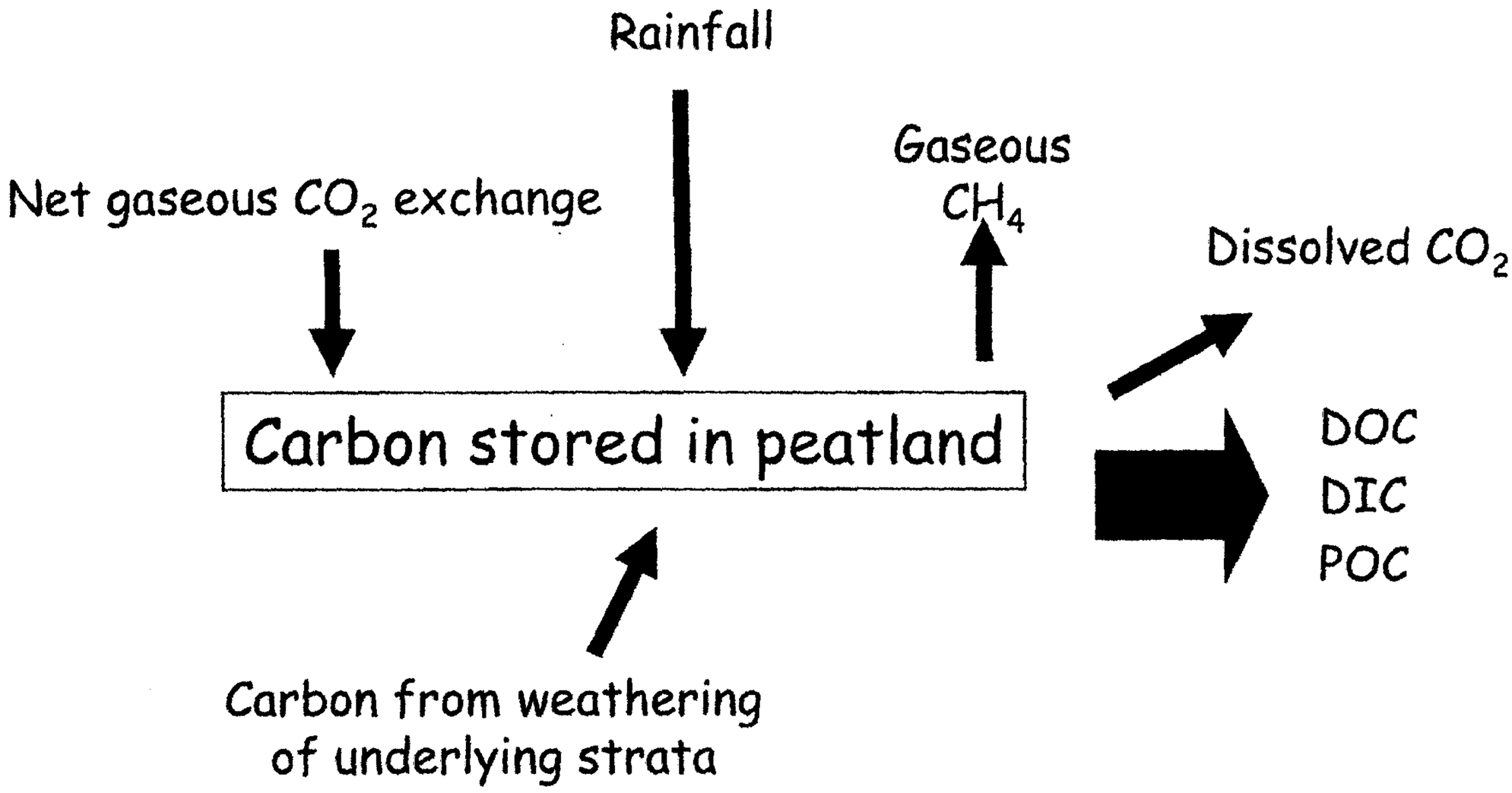

Figure 5.1 Carbon exchange pathways (Worrall *et al.*, 2003)

Carbon fluxes are not measured continuously in this thesis, and a carbon budget calculation is based upon predicting carbon fluxes by using intensively monitored driver variables which include; soil, air and water temperature, PAR, and water table depth. This leads to the question of: What is the lowest level of monitoring which still give a good estimate of the carbon budget at Hexhamshire Common field site?

In the diagram by Worrall *et al.*, 2003 (Figure 5.1), different pathways loose different amounts of carbon, therefore the different losses of carbon can be compared and the question: Which gaseous pathway looses the greatest amount of carbon, can be asked.

Once the best estimate of the carbon budget for the field site has been calculated this will answer the question of: Has the Hexhamshire Common field site turned from a sink into a source of carbon, based upon either best estimate flux formulae or statistical estimates of

the carbon flux budget.

Having calculated the carbon budget for the Hexhamshire Common field site it is appropriate to ask: Which is the best method for calculating a carbon budget for an upland peat field site and which factors need to be measured.

Once a carbon budget estimate has been calculated, the equations used to predict the carbon fluxes during times when carbon fluxes were not measured needs to be discussed.

5.2. Introduction to Field Sites

Readings of gaseous CO_2 were collected from Hexhamshire Common field site, which is located on the North Pennies on upland peat approximated 25 miles west of Durham City. For a full description of the field site and the measurements made refer to Chapter 2, section 2.3, Methods.

5.3. Objectives and Hypotheses

The objectives of this chapter are:-

1. What is the lowest level of monitoring that still gives good estimates of carbon budgets at the Hexhamshire Common field site?

2. Has the Hexhamshire Common field site turned from a sink into a source of carbon, based upon either best estimate flux formulae or statistical estimates of the carbon flux

budget?

3. Which gaseous pathway loses the greatest amount of carbon, and which gains the greatest amount of carbon, if any?

4. Which is the best method for calculating a carbon budget for a field site and which factors need to be measured?

5.4. Methods

In hydrological literature there are extensive reviews on the calculation of mass load balances in stream river beds, and are related to concentration and stream discharge (Meunier *et al.*, 2006; Cooper *et al.*, 2002; Rondeau *et al.*, 2000; Littlewood *et al.*, 1998; House *et al.*, 1997). In carbon cycle literature there are few comparisons of carbon budget calculations, the different methods used to calculate the carbon budgets, and the different gap filling approaches used to calculate fluxes between measured samples, and how representative these samples are compared to the year as a whole (Worrall *et al.*, 2003). There is also little discussion of the time periods involved in the modelling of a carbon budget, and how averaging continuously monitored, highly variable data, affects the outcome of a carbon budget estimation. Using mass balance equations from hydrological literature and applying them to carbon budget calculations should give an unbiased estimation of the losses and gains of carbon from a field site.

Using the data collected, and discussed in chapters two and three, of different gaseous and dissolved flux values over a years time period, two mass balance approaches were

used to estimate the carbon budget for the field site; an extrapolation approach and an interpolation approach. Briefly, an interpolation approach takes flux data that has been measured over a year and calculates the sum of these values and discusses how representative these samples were over the time period, compared to how representative these samples were against highly monitored drivers such as PAR, flow and soil temperature (Hilbert *et al.*, 2000). An extrapolation approach takes the highly measured driver variables, again such as PAR, flow and soil temperature, and uses them to predict what the fluxes should be, and from this data a carbon budget is calculated (Langeveld *et al.*, 1997). These two methods will then be compared against each other to find how representative each method is.

The equations that were used for assessing annual mass load for fluvial fluxes are taken from Littlewood *et al.*,(1998).

$$L_2 = K \frac{\left(\sum_{i=1}^{n} (Q_i C_i) \right)}{n} \qquad \textbf{5.i}$$

Where, Q_i = flow corresponding to a sample taken on day i, and C_i = concentration of the interested species in an instantaneous sample taken on day i. n = number of samples taken during the sampling period. K = number of hours in sample period (normally a year). This is the so called 'Method 2' (Littlewood *et al.*, 1998).

An alternative approach is called 'Method 5' (Littlewood *et al.*, 1998) paper, and is more complex and looks at how representative the concentration samples are by comparing

them to the representativeness of the flow samples.

$$L_5 = \frac{\sum_{i=1}^{n}(Q_i C_i)}{\sum_{i=1}^{n}(Q_i)} Q_y \qquad \text{Where } Q_y = \frac{\sum_{k=1}^{N} Q_k}{N} \qquad \textbf{5.ii}$$

Where, Q_i = instantaneous flow measurement taken at the same time that the concentration measurement (C_i) was taken. Q_k = daily mean flow for each day of the year. N = number of years in sampling set. The third and final equation, called 'Method A', applied to the data, again taken from Littlewood *et al.*, (1998), is the estimation algorithm:-

$$L_A = \sum_{j=1}^{n-1} \frac{1}{2} \sum_{i=1}^{2} C_{i,j} \frac{K_j \sum_{k=1}^{m_j} Q_{k,j}}{m_j} + \text{start} + \text{finish} \qquad \textbf{5.iii}$$

Where, $C_{i,j}$ = instantaneous concentration in the jth segment. K_j = the number of seconds in jth segment. $Q_{k,j}$ = Kth value of the daily mean flow in the jth segment. m_j = number of daily mean flows in the jth segment. Start and Finish = estimate the mass of material carried by the river at the start and finish of the sampling period. This equation is based on equation 5.ii, but takes into account of aperiodicity in concentration data.

5.4.1. Applying the formulas to gaseous carbon budget fluxes.

To calculate the carbon budget for Hexhamshire Common field site the formulas from Littlewood *et al.*, 1998 need to be interpreted in relation to the values that have been measure in this project. The total gaseous carbon budget for the site is the Net Ecosystem Exchange (NEE). This is a combination of the amount of carbon taken up by plants, or Primary Productivity (PP) against the amount of carbon released by respiration processes of the soil and plants (R). Or in an equation format:-

$$NEE = PP + R \qquad \textbf{5.iv}$$

Although this equation seems simple it can be broken down to reveal much greater complexity. The total amount of CO_2 released by peat respiration is a combination of heterotrophic and autotrophic organisms. Whilst primary productivity is the total amount of CO_2 taken up by the plants, dependent upon different driving functions such as PAR, air temperature, soil moisture, and available nutrient, and atmospheric CO_2 concentration. This still is not the end of the breakdown as below ground respiration can be broken down into different pools of carbon such as leaves, woody roots, fine roots, and understory/herbivory, and autotrophic respiration (Curtis *et al.*, 2002). Different plants have different rates of uptake of CO_2, and different plants will promote respiration and others will inhibit respiration. Fortunately, in this project, the above variables can largely ignored because of the way the gases fluxes were measured. This is because a closed chamber was used to measure all of the below ground respiration in a single measurement, and could not distinguish between the different types of respiration from

heterotrophic and autotrophic microbes. A closed chamber method is also unable to determine which carbon source the CO_2 gas has come from, but has the advantage of measuring all the CO_2 release by all of these different sources. Different plant uptake rates can also be largely ignore by using a closed chamber because the plants are physically constrained within the chamber, and the amount of CO_2 taken up by the plants will depend upon the sunlight levels during the measurement period. As the measurements of NEE were repeated both spatially and temporally, this averaged out any changes in plant type.

The first equation applied to the measured fluxes is Equation 5.i. This equation becomes:-

$$NEE_{year} = K \frac{\sum_{i=1}^{n} (R_i + PP_i)}{n} \qquad \textbf{5.v}$$

Where NEE_{year} = total amount of Net Ecosystem Exchange for the year. K = number of hours in the year, R_i = instantaneous flux measurement of respiration, PP_i = instantaneous flux measurement of primary productivity. n = number of samples taken. This approach gives a basic average of the overall carbon budget of the Hexhamshire Common field site. Methane fluxes can also have Equation 5.i applied, again giving a basic overall average of the methane flux, which will be presented in the results section.

From Chapter 2, it was concluded that the best way to predict carbon fluxes from the site

was to combine two literature methods from Lloyd *et al.,* 1994 (See Equation 5.vi), and Bubier *et al.,* 2003 (See Equation 5.vii), to predicted gross flux and net flux respectively.

$$R = R_{10} e^{E_o\left(\left(\frac{1}{283.15-227.13}\right)-\left(\frac{1}{T_{soil}-227.13}\right)\right)}$$

5.vi

$$NEE = \left(\frac{GP_{max} \times \alpha \times PAR}{\alpha \times PAR + GP_{max}}\right) + R$$

5.vii

In this thesis, the question of what is the lowest level of monitoring that still gives a good estimate of flux from the field site, will be answered by manipulating these equations. From the driver functions defined by Lloyd *et al.,* 1994 (Equation 5.vi) and Bubier *et al.,* 2003 (Equation 5.vii) and using the 15 minute data sets of soil temperature and PAR, different monitoring regimes can be defined and used to predict the flux from the field site to see what variation in the carbon budget different monitoring regimes can give.

5.4.2. Applying the formula to dissolved gaseous fluxes

The equations 5.i to 5.iii from Littlewood *et al.,* (1998) can be applied to dissolved gaseous fluxes, treating dissolved CO_2 as a fluvial flux.

According to equation 5.iii, several different time periods can be used to define the jth segment time period. As flow was measured on a 15 minute interval, different monitoring regimes can be defined, and these values used in 5.iii to estimate the carbon

export from the site.

Different catchment size areas will have different flow regimes depending on the amount of rain a catchment receives and the area of the catchment. The above equations by Littlewood *et al.*, (1998) will only give the total carbon export for a catchment to make the catchments comparable the total carbon export will be divided by the area of the catchment.

5.5. Results

5.5.1. Gaseous net and gross CO_2 flux budgets

Calculating the carbon budgets for the Hexhamshire Common field site by different methods inevitably leads to different answers, the question is how much and why they differ. One difference in the data may have occurred due to the type of method used to collect net gaseous CO_2 data. For example, there were two different methods used to measure CO_2 concentration; a clear acrylic, purpose built chamber, and a series of cloches made with clear acrylic tops and opaque walls. These two different methods of measuring net CO_2 fluxes gave a non-concurrent data range when analysed statistically using multiple linear regression with soil temperature and PAR as variables (For a full discussion see chapter 2). The reason for this difference was that the clear acrylic chamber had a PAR probe within the chamber and the amount CO_2 uptake could be directly compared with the PAR levels within the chamber. The cloche chambers

probably reduced the light levels within the chamber to a greater extent than the acrylic chamber, therefore plants would have photosynthesised less, but as the only measure of PAR when using the Cloche chambers was an external PAR probe no direct comparison between the PAR levels within the chamber and net CO_2 flux could be made. This observation is justified when analysing the gross data, and the differences between the two chambers, it was found that the gross flux data for both chamber types was statistically the same when compared to the main driving variable of soil temperature. This would mean that the net flux data measured from the cloches should be anomalously biased towards the gross fluxes, by underestimating the amount of carbon taken up by net fluxes. This meant that if all the measured data from both chamber types was used then it would give an anomalously high carbon release value for the field site. Using this method it gave a total value of 36.7 tC $Km^{-2}a^{-1}$. Assuming that there is a bias towards gross flux data by using the cloche data and simply excluding the net flux data from cloches gives a new estimate of -6.2 tC $Km^{-2}a^{-1}$ for net flux and 128.8 tC $Km^{-2}a^{-1}$ for gross flux. When compared to the best estimate of gross flux of 189.9 tC $Km^{-2}a^{-1}$ shows that excluding the data from the cloches underestimates the gross fluxes by 32%. Applying the same underestimate to net fluxes predicts a net flux uptake of -8.1 tC $Km^{-2}a^{-1}$. The best estimate of net flux from the field site predicts that the field site is a source of 17.7 tC $Km^{-2}a^{-1}$. Therefore, the estimate of net flux by excluding the cloche data is unlikely to be an accurate estimate of net flux because this would assume a linear relationship between soil temperature and gross flux; soil temperature, PAR and net flux. As can be seen from the Lloyd *et al.*, (1994) equation (Equation 5.vi) and Bubier *et al.*, (2003), equation 5.vii neither of these equations predict a linear relationship between the

driver variables (PAR and soil temperature) and flux. Therefore, it is not valid to simply discount the cloche data from the carbon budget estimate.

5.5.2. Precision using different time periods

To answer the question of; what is the lowest level of monitoring the still gives a good estimate of the carbon budget several different monitoring regimes need to be defined. The first, and which gives the best estimate of flux from the site, is predicting the carbon budget using the data from the 15 minute data set using the Lloyd and Taylor (Equation 5.vi) and Bubier equation (Equation 5.vii). This gives an estimated net carbon release of between 17.7 and 28.5 tC $Km^{-2}a^{-1}$, and a gross release of between 181.4 and 189.9 tC $Km^{-2}a^{-1}$. The next monitoring regime would be to predict flux using a daily average of soil temperature and PAR. Using a daily average of soil temperature and PAR gives a net carbon budget of an uptake of 70.7 (-70.7) tC $Km^{-2}a^{-1}$, with a gross release of 189.5 tC $Km^{-2}a^{-1}$. As can be seen from the best estimate flux values and daily averages estimates of flux, the net fluxes from the field site are poorly correlated with a difference of between 89.4 and 100.2 tC $Km^{-2}a^{-1}$ so it can be said that average daily PAR values do not provide a good estimate for predicting net fluxes. However, the gross fluxes can be said to be in good correlation with a small difference of 0.39 tonnes of carbon. The difference between the two results, net being poorly correlated and gross being well correlated, could be explained by the amount of variability within the driver data sets i.e. the variance within PAR, and the variance within soil temperature, for each day. Soil temperature has a much smoother daily temperature range so the standard deviation of

daily soil temperature should be smaller than the daily standard deviation of daily PAR values as PAR is much more irregular in its daily profile and will be affected by both diurnal cycles and cloud formation. The standard deviations of specific days for PAR and soil temperature in winter, spring, summer and autumn can be seen in the table below:-

Season	Standard deviation of select days PAR values	Standard deviation of select days soil temperature
Winter	33.0	0.87
Spring	125.4	0.51
Summer	567.1	0.67
Autumn	233.1	0.32

Table 5.1 Standard deviations of PAR and soil temperature values of certain days in each season

As can be seen from Table 5.1, the standard deviations of soil temperature and PAR are greatly different with PAR having a much larger values, thus having greater variance within the data set, and it has been shown that an average of the daily PAR values is not a good predictor of net flux.

The next monitoring regime, similar to taking a daily average, finds a representative time of day to take both soil and PAR readings. This is not the same as taking an average as discussed above as daily average PAR values are not appropriate in calculating net flux

values as plant response to PAR is not linear. Using specific soil temperature and PAR values from certain times of day and multiplying the flux up to yearly values shows that the best time to take soil temperature and PAR readings is between 6:45am and 7:15am as shown by Table 5.2.

Collar Number	Time; 6:45am	Time; 7:00am	Time; 7:15am
1	2.280	-16.19	-37.327
2	150.0	149.8	149.6
3	-9.7	-28.6	-48.8
4	478.7	130.4	130.3
5	-9.6	-39.4	-70.9
6	219.2	218.9	218.7
7	163.5	152.3	139.8
8	235.4	235.1	234.9
Total collars net	36.6	16.9	-4.3
Total collars gross	183.8	183.7	183.4

Table 5.2 Predicting yearly net and gross flux from specific times of day (tonnes C $m^{-2}a^{-1}$)

As can be seen from Table 5.2, the time which estimates the net fluxes according to the best estimate is 7:00am (GMT), for both net and gross flux. Gross flux is also accurate for the other two times calculated; again this is due to soil resistance to temperature change. For the net fluxes the error can be seen to be quite large and because the data set is only for a year it is not known if this relation holds for longer than this.

The third monitoring regime is to taking weekly averages of soil temperature and PAR this should average out the variation within the PAR levels, and give a longer term average.

Collar Number	Yearly carbon budget (tonnes C $Km^{-2}a^{-1}$)
1	-103.1
2	137.1
3	-108.2
4	119.4
5	-171.7
6	200.4
7	-444.0
8	215.2
Total collars net	-206.8
Total collars gross	168.0

Table 5.3 Predicting carbon budget using weekly average values of soil temperature and PAR

As can be seen from Table 5.3 net flux is hugely over estimated, compared to the best estimate of flux, and the amount of over estimation is greater than predicting the net flux from the site using daily averaged values. This suggests that finding a representative time of day is a poorer method for calculating flux values than either daily averaged values or using the 15 minute data set values. The total gross fluxes from the field site

can, again, be seen to be in good agreement with the best estimate of gross flux from the field site, although the underestimation of gross flux has increased from prediction flux using daily averaged values. This show that as the time scale becomes longer in the monitoring regime the error increases, with the model overestimating net fluxes and underestimating gross fluxes as the time between measurements increase, and averaging periods increase.

5.5.3. Dissolved gaseous CO_2 flux budgets

Dissolved CO_2 export from each of the 5 catchments (Hex1, Hex 2, Hex 3, Cowgreen, and Widdybank) estimated using the above methods (Block, L_2, L_5, and Method A) can be summarise in the following table (Table 5.4)

Method	Hex 1	Hex 2	Hex 3	Cowgreen	Widdybank
Block	5.3	38.4	10.9	13.7	161.7
L_2	5.9	37.5	8.8	13.6	245.8
L_5	4.4	51.5	9.7	17.6	165.1
Method A	5.2	51.0	15.9	27.4	161.2

Table 5.4 Carbon export for each catchment (kgC a^{-1})

From Table 5.4 it can be seen that the Widdybank catchment has a much large catchment compared to the other catchments, this is to be expect as Widdybank has a much larger catchment area, thus draining a large area of peat and exporting more water from the catchment. As shown from Chapter 3, the amount of carbon exported from these catchments is related to the water export from each catchment. Make the results

comparable by dividing the export figures by the area of catchment gives the following table (Table 5.5)

Method	Hex 1	Hex 2	Hex 3	Cowgreen	Widdybank
Block	3.0	5.1	3.9	3.9	5.88
L_2	3.3	5.0	3.9	3.9	8.9
L_5	2.9	6.8	6.6	7.8	5.86
Method A	2.9	5.9	4.7	5.2	6.7

Table 5.5 Yearly dissolved CO_2 flux (gC $m^{-2}a^{-1}$)

Graphically, the different carbon fluxes estimated by the different methods (block to Method A) shows the differences in figures for the different methods (Figure 5.2).

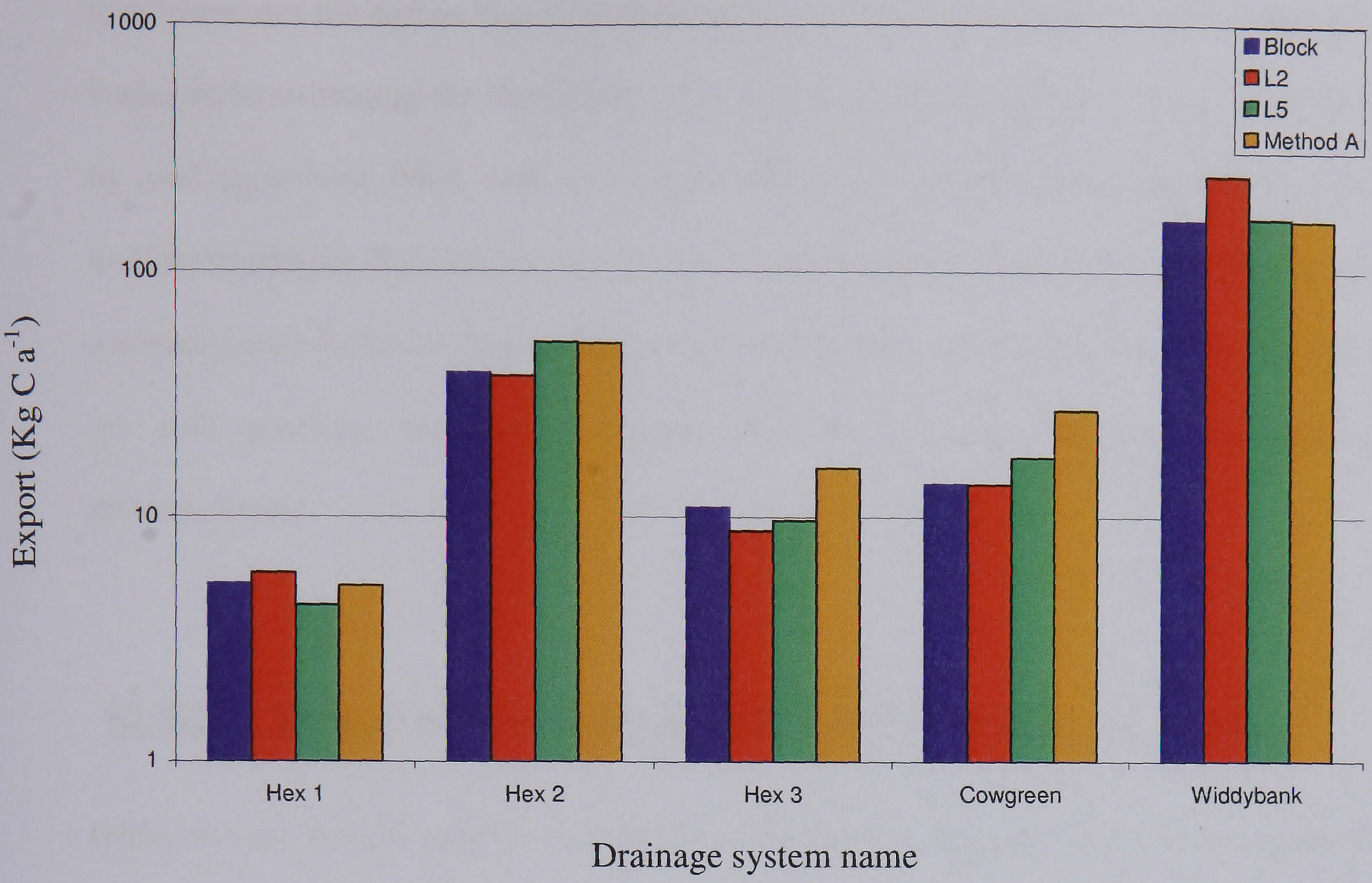

Figure 5.2 Graph comparing different estimates of carbon export

As can be seen from Figure 5.2 all the estimates of flux are in good agreement with each other with none of the flux estimates varying widely. According to Littlewood *et al.*, (1998) the best estimate of dissolved flux is method A, which is a mass load estimation algorithm which takes into account of aperiodicity in concentration data. With this method there are known problems discussed in Littlewood *et al.*, (1998), the main problem being the assumption that the appropriate mean flow for each of the periods is the average of the m_j daily mean flow in the jth segment. Assuming method A is the best estimate of carbon flux, comparing the other methods for flux estimation to the values estimated using method A shows that the block estimation method consistently underestimates the carbon fluxes for all sites. The L_2 method both overestimates and

underestimates the carbon fluxes, overestimating the fluxes from Hex 1 and Widdybank, whilst underestimating the fluxes from Hex 2, Hex 3, and Cowgreen. The L_5 method is in good agreement when used to estimate the fluxes for Hex 2 and Widdybank, but underestimates the fluxes from Hex 1, Hex 3, and Cowgreen. It is unknown whether it is a coincidence but the catchments that are allowed to drain freely (Hex 2 and Widdybank), are well predicted by the L_5 method, and the blocked catchments are always underestimated.

5.5.4. Precision using different time periods

Different time periods used for calculating carbon export from the field site is considered by the type of equation used. In Littlewood *et al.*, (1998), the equations L_2 and L_5 (Equation 5.i, and 5.ii) are the same when n = N. However as sampling frequency increases to greater than daily sampling, as in this thesis, error increases. The question is by how much and which equation gives the better precision. Littlewood *et al.*, (1998), determined that L_5 gave a better precision when using a computational framework to estimate the concentration of nitrate over a representative period of flow.

When concentration data is not taken at regular intervals, the data will show aperiodicity, this is the case with the data in this thesis because of the land owners wishes, and dissolved CO_2 was measured with a much greater frequency during winter months than during summer months. According to Littlewood *et al.*, (1998), method A (Equation 5.iii) takes this into account and will provide a more accurate estimate of carbon export.

5.5.5. Pathway losing the greatest amount of carbon

To answer which pathway loses the greatest amount of carbon, and which gains the greatest amount of carbon, if any, a simple comparison of the gaseous and dissolved CO_2 fluxes will answer this question.

To make the results comparable, the collars closest to the blocked and unblocked grip will be used, as well as the overall net and gross gaseous carbon budgets from the field site.

The overall loss of gaseous carbon from the field site is 17.7 tC $Km^{-2}a^{-1}$, the average loss of carbon as dissolved excess CO_2 from each of the three Hexhamshire Common grips is 0.02 tC a^{-1}. As can be seen from these figures, the gaseous loss of CO_2 is much greater than the dissolved CO_2 loss. There is large variation between the amount of carbon lost from a blocked and unblock grip, so the gaseous flux of carbon can be broken down into their respective collars. Collars 3 and 4 have the shallowest water table depth for all of the collars across the transect. Therefore, it is reasonable to say that all water on the collar 1 and 2 side of collars 3 and 4 will run to the unblocked grip, and all other waters between collars 3 and 4 and 7 and 8 will run into the blocked grip, see chapter 3 section 3.4.6, for justification. Therefore, it can be assumed that the average of the gross fluxes for collars 6, and 8 will be the CO_2 producers which contribute to the dissolved CO_2 in

the blocked grip and collar 2 will contribute to the dissolved CO_2 in the unblocked grip. The greater the amount of carbon fluxing from the surface of the peat as gaseous carbon will mean that less CO_2 will be dissolved in the soil pore water and so contribute to the excess partial pressure of CO_2 within the grip. The reverse is also true, the greater the amount of carbon dissolving into the soil pore water, the less carbon will flux from the surface of the peat. As has been shown above, the unblocked grip exports more carbon than the blocked grip (51.0 and 15.9 KgC a^{-1} respectively), and collar 2 releases less carbon than an average of collars 6 and 8 (155.0 and 234.9 tC $Km^{-2}a^{-1}$ respectively). A hypothesis in chapter 2 stated that the lower the water table the greater the CO_2 flux from the surface of the peat. Using the fact that an unblocked grip releases more carbon than blocked one, this hypothesis could be modified to:- A low water table will produce a certain amount of CO_2 and this will be lost either gaseously or dissolved in soil pore water, and exported from the site via the field site drainage system. This would mean that the sum of the gaseous CO_2 fluxes and dissolved CO_2 fluxes should be a constant for a given water table depth and soil temperature. This was only proved in Chapter 4, where is was found that there was a relationship between water table depth and that the Lloyd and Taylor equation better predicted the variation in the gross CO_2 release

5.6. Discussion

As can be seen from the results section there are several estimates of carbon budget values and these values vary considerably for both gaseous and dissolved gasses. The best estimate of gaseous carbon flux from the field site is provided by combination of the

Lloyd and Taylor equation (Equation5.vi) and the Bubier equation (Equation 5.vii). To give a net flux of 17.7 tC $Km^{-2}a^{-1}$ and a gross flux of 189.9 tC $Km^{-2}a^{-1}$. The best type of chamber to use to accurately predict net fluxes was a purpose built acrylic chamber which let in more light than a series of cloches. The chamber type did not matter when measuring gross fluxes, and a series of chambers which could be left on the soil surface for longer in cold periods will provide a more accurate estimate of gross flux than an individual chamber measuring a time series of gross CO_2. It is not justifiable to exclude the driver variable data (soil temperature and PAR) from the period of the year when the cloches were used as this over estimates the amount of carbon taken up by the plants.

Changing the time period over which the flux formulae are applied, for example, averaging data to daily and monthly values, all gave different carbon budget values, and they often overestimated the actual carbon budget of the site compared with the best estimate of flux from the field site. What justification is there that the best estimate carbon budget from the field site is a valid figure? A counter argument for using fifteen minute data set is that the plants primary productivity and peat respiration will not respond quickly enough to be affected by small changes in PAR and soil temperature. However, looking at the original CO_2 concentration data measured by clear acrylic chamber, which made measurements of PAR and CO_2 concentrations every 4-5 seconds, and looking at a partially cloudy day, with a brisk breeze, meaning PAR levels will change regularly, showed that the CO_2 concentration (ppmv) within the chamber changed according to changes to PAR levels (This measurement was not included in the net flux data, and the measurement was retaken when PAR was constant):-

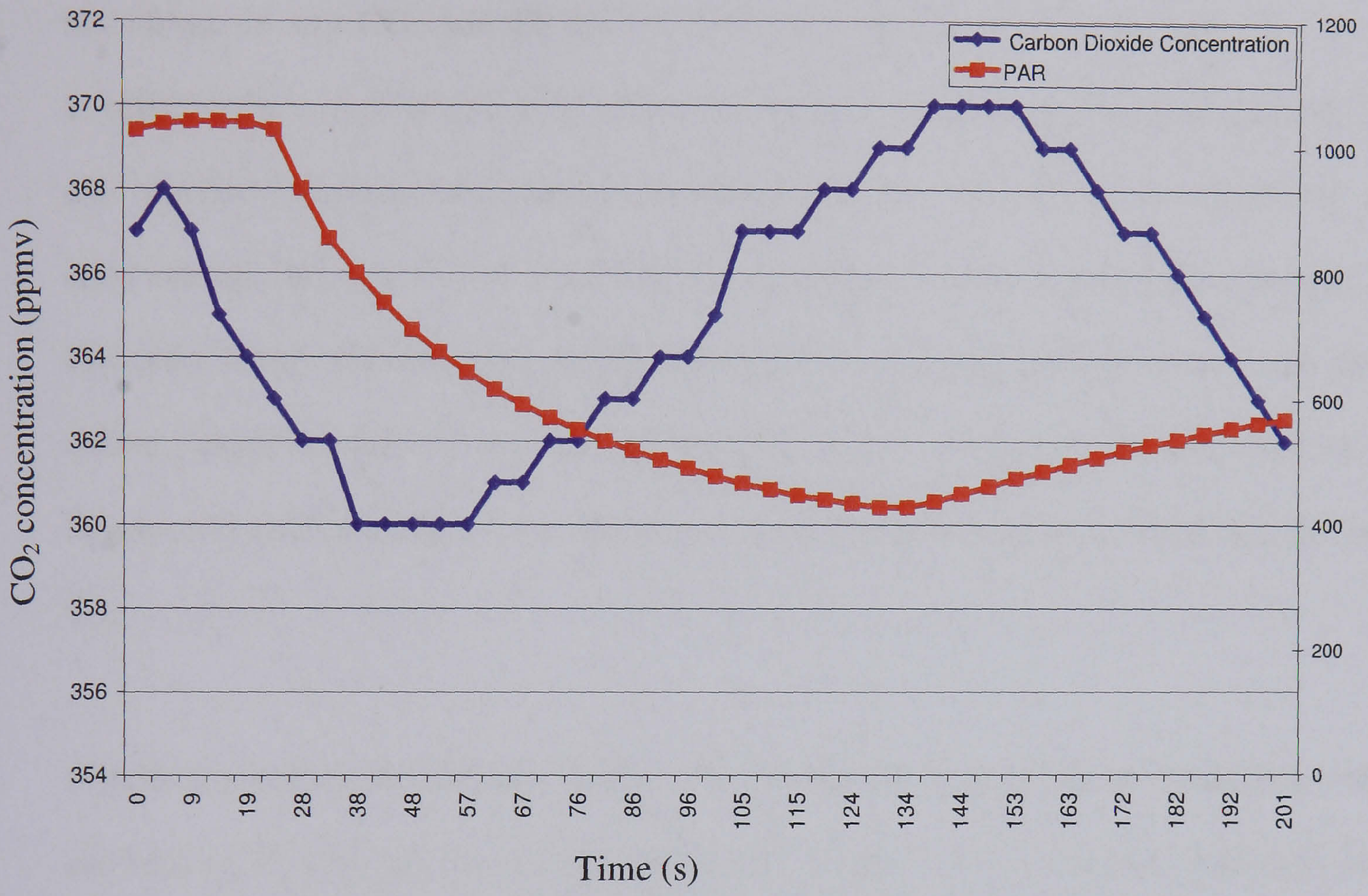

Figure 5.3 CO_2 change within the chamber according to PAR levels

This justifies the use of the 15 minute data set showing that plants will respond quickly enough to changes in PAR levels.

Averaged daily values of PAR did not give a good estimate of net flux from the site and over estimated the amount of CO_2 taken up by the plants when compared to the estimated flux from the 15 minute data set. The reason for this is that the relationship between the plants and PAR is not a linear one and the rate of CO_2 taken up by the plants will plateau as PAR increases and no longer become the rate limiting step and another factor becomes

a rate limiting step such as soil moisture. Averaged daily values of PAR also take no account of diurnal variations, as on average, there are 12 hours a day when the plants are not taking up any CO_2 and the peat is still respiring CO_2. The advantage of using averaged daily values of soil temperature and PAR is that although logging equipment will needed to monitor instantaneous soil temperature and PAR levels and calculating a daily average, the logger can be left for longer without the need for downloading the data. The same is true of weekly and monthly average data. However, as can be seen from the carbon budget estimates using these weekly and monthly averaged values, net flux was largely over estimated the net carbon flux and under estimate the gross carbon flux (Table 5.3).

If there is not the facility for data loggers, then the lowest level of manual monitoring that can be done are daily readings of soil and PAR at 7:00am. This is a statistical analysis of the data and as the results were measured over one year, it is unknown whether this is the preferred time for more than one year. Another disadvantage with this level of monitoring is the time it takes to collect flux readings, if 7:00am is taken as an accurate time to measure the net and gross fluxes. Using the clear acrylic chamber to take the readings and taking measurements over a 2 – 5 minute period measuring a minimum of eight collars will take a minimum of 25 minutes when the minimum measurement times were used. Allowing for self calibration by the IRGA and purging the chamber in between measurements up to a maximum measurement time of an hour. As can be seen from the times either side of the 7:00am time (6:45am and 7:15am) showed large changes in predicted net flux values, and if taking net and gross flux readings takes longer than

this short time frame then the results can be said to be none representative of the net and gross fluxes from the site. However if just soil temperature and PAR are being measured at 7:00am then this can be comfortably done within the time frame, but no flux readings can be collected to confirm that this is indeed a representative time of day to take flux readings. Therefore a better approach would be to measure flux readings from a site and then used those results to calibrate the constants for the Bubier *et al.*, (2003) formula, and estimate a representative time of day to measure PAR and soil temperature.

When estimating the dissolved CO_2 fluxes for the site, Littlewood *et al.*, (1998), concluded that the best method for calculating a flux from a site was method A which takes into account aperiodicity within the data. When compared to three other methods for predicting flux it was found that all the methods were in agreement with each other at the same order of magnitude. Compared to the best estimated of dissolved flux over time using method A the other methods generally underestimate the fluxes.

Whilst it has been proved that there is not a constant amount of CO_2 being released from the peat, there is a relationship between the gaseous and dissolved CO_2 fluxes, and is link to water table depth and soil temperature (See chapter 4). Carbon dioxide is produced in soil pore spaces, and will equilibrate with the soil pore water, it then depends on the pathways available, whether the CO_2 in the peat will be released gaseously or hydrologically. The CO_2 can; remained trapped in the soil pore spaces, flux directly to the surface if there is a pathway available, flux to the surface after a pathway opens in the peat due to drying, flux to the surface via plant roots, be flushed out of the peat due to

water flow, either during a rainfall event or due to drainage, force CO_2 to the surface by a rising water table. From these different pathways it can be seen that rainfall should affect the amount of rain that fall as this will flush dissolved CO_2 into the drainage system, force CO_2 to the surface due to a rising water table. From statistical analysis it has been proved that rainfall does not have an effect on the amount of CO_2 fluxing from the peat surface (Chapter 2). To prove a relationship between rainfall and CO_2 flux, measurements would need to be made continuously whilst a rainfall event was occurring and immediately afterwards, as it is unknown how soon after a rainfall event there would be; an increase in gross CO_2 flux, or even if there is an increase in gross fluxes. Other factors which may affect the CO_2 fluxes are; the magnitude of a rainfall event, the duration, and the time between rainfall events. All of these factors will influence the amount of gross CO_2 fluxing from the peat surface. It is also inappropriate to use a flux tower to make this type of measurement as one of the main instruments used in calculating net CO_2 flux from the peat surface is a sonic anemometer, which measures the speed of sound in three dimensions. This instrument is badly affected by rainfall and moisture in the air as water droplets collect on the end of the instrument tips, and affects the measure of the speed of sound in air if it has to pass through the water droplets first, and will give a lower flux value of CO_2 flux, and often these results are discarded from eddy covariance measurements, so any large fluxing of CO_2 due to rain fall events is not seen. Flux towers are also not used in grips areas because flux towers need to be sited in an area that is homogenous and flat. If an area is flat and homogenous then it cannot have grips, and dissolved CO_2 samples cannot be collected.

5.7. Conclusions

In conclusion the required level of monitoring for the field site for an estimate of CO_2 flux is 15 minute average data set for soil temperature and PAR levels. These values will provide a good estimate of the net and gross gaseous fluxes from the field site. The lowest level of monitoring of dissolved CO_2 fluxes from the field site are continuous measure of flow to provide both instantaneous flow and daily average values. Systematic and frequent concentration measurements of dissolved CO_2 over a year will provide an accurate estimation of the dissolved fluxes of CO_2. There has to be some measure of the concentration of dissolved CO_2 throughout the year, the less frequent the measures, the larger the error will be.

From the best estimate values of net flux of gaseous CO_2 shows that the site is a source of 17.7 tC $Km^{-2}a^{-1}$. Which is a small but significant number as it means that this upland peat is loosing carbon, and is no longer a sink of carbon. It can also be shown that the field site is an average source of 24.0 KgC a^{-1} of dissolved CO_2. It has also been shown that unblocked grips export more carbon than blocked grips, therefore blocking grips can be used as a carbon preservation technique.

The pathway that looses the greatest amount of carbon is via direct CO_2 loss from the surface of the peat. It is also hypothesised that the amount of dissolved CO_2 exporting from the site has an effect on the amount of CO_2 fluxing from the surface of the peat.

The best method for calculating gaseous CO_2 flux from the site is using the Bubier equation (Equation 5.vii) with Lloyd and Taylor's equation (Equation 5.vi) to estimate gross flux. The best method for estimating the dissolved CO_2 export, is Littlewoods *et al.*, (1998) method A, which is based on flow and measurements of dissolved CO_2 concentration over time.

6. Introduction to Eddy Covariance, using a flux tower

An introduction to setting and siteing a flux tower. An introduction to the equations used in micrometeorology. A study of the diurnal and seasonal nature of CO_2 fluxes.

6.1. Introduction

For some years there has been increasing interest in measuring the transfer of CO_2 and other minor gaseous constituents in the atmosphere (Webb et al 1980). One of the first and easiest ways of measuring these fluxes was using small spatial scale readings of field sites using open or closed path chamber measurements, for example see chapter 2. However, these were limited to small spatial and temporal scales with the inability to take readings rapidly enough over a large enough area to accurately measure carbon fluxes, and only estimates could be obtained. Another problem with this method is that placing the chamber on the vegetation surface will alter the local environment around the sample by compressing and warming the surface, and possibly giving a non-representative sample of the surface. With the advent of eddy covariance measurements long term eddy covariance sites, measuring carbon and energy fluxes, provided a unique contribution to the study of the environmental, biological, and climatological controls of net surface exchange between vegetation and the atmosphere (Baldocchi et al., 2001). Eddy covariance measures of CO_2 fluxes, can be compared to closed chamber methods and

determine whether the CO_2 fluxes are comparable. Other studies have compared eddy covariance fluxes with CO_2 fluxes of which the most comparable to this study is the study by Laine *et al.*, (2006). Laine *et al.*, (2006) measured CO_2 flux by both eddy covariance and closed chamber, and concluded that there was a poor correlation between closed chamber measurements and eddy covariance measurements on a short time scale, but with good correlation on a long time scale. The advantage of eddy covariance when measuring CO_2 flux is that CO_2 can be measured continuously both day and night whereas closed chamber measurements of CO_2 flux can only measure diurnal cycles of CO_2 flux on a campaign basis. Therefore, it is proposed that if there is a good correlation between the eddy covariance measures of CO_2 flux and the closed chamber method, and a diurnal cycle can be established, then a correction factor could be applied to the closed chamber measurements when a carbon budget is calculated for the site.

Carbon released as CO_2 and measured at a flux tower as a concentration in mg m^{-3} is an almost meaningless number without proper processing, and a suite of other measurements. For an introduction to the theory and the equations used in eddy covariance see appendix 3.

6.2. Aims and Objectives

1. To quantify the CO_2 fluxes from an upland peat using eddy covariance methods

2. To determine whether the magnitude of these fluxes are the same as IRGA readings taken on similar peat land approximately 18.1km to the north east.

3. To determine the range of diurnal cycles for CO_2 fluxes

4. Investigate a correction factor between large scale diurnal CO_2 flux measurements and small scale IRGA readings.

6.3. Methods

6.3.1. Site Description

The Moor house field site is located 51.5 kilometres west of Durham City on the North Pennines at grid reference; NY 76095, 33090. The field site is 562 meters above sea level. The underlying geology of Moor house is succession of Carboniferous Limestones, sands and shales, with intrusions of doleritic Whin Sill (Johnson *et al.,* 1963; Worrall *et al.,* 2003). The Moor house field site has been classified according to the National Vegetation Classification (NVC), as an M19 Calluna Vulgaris – Eriophorum Vaginatum blanket mire. The main plant species are *Sphagnum Capillifolium, Sphagnum Papillosum, Polytrichum Commune, Eriophorum Vaginatium* and *Calluna Vulgaris,* with infrequent *Pleurozium Schriberi, Hypnum Jutlandium, Erica Tetralix, Rubus Chamaemorus, and Drosera Capillaris.* For a location of the Moor house site, see Chapter 3 section 3.3.1, figure 3.1.

6.3.2. Flux tower setup

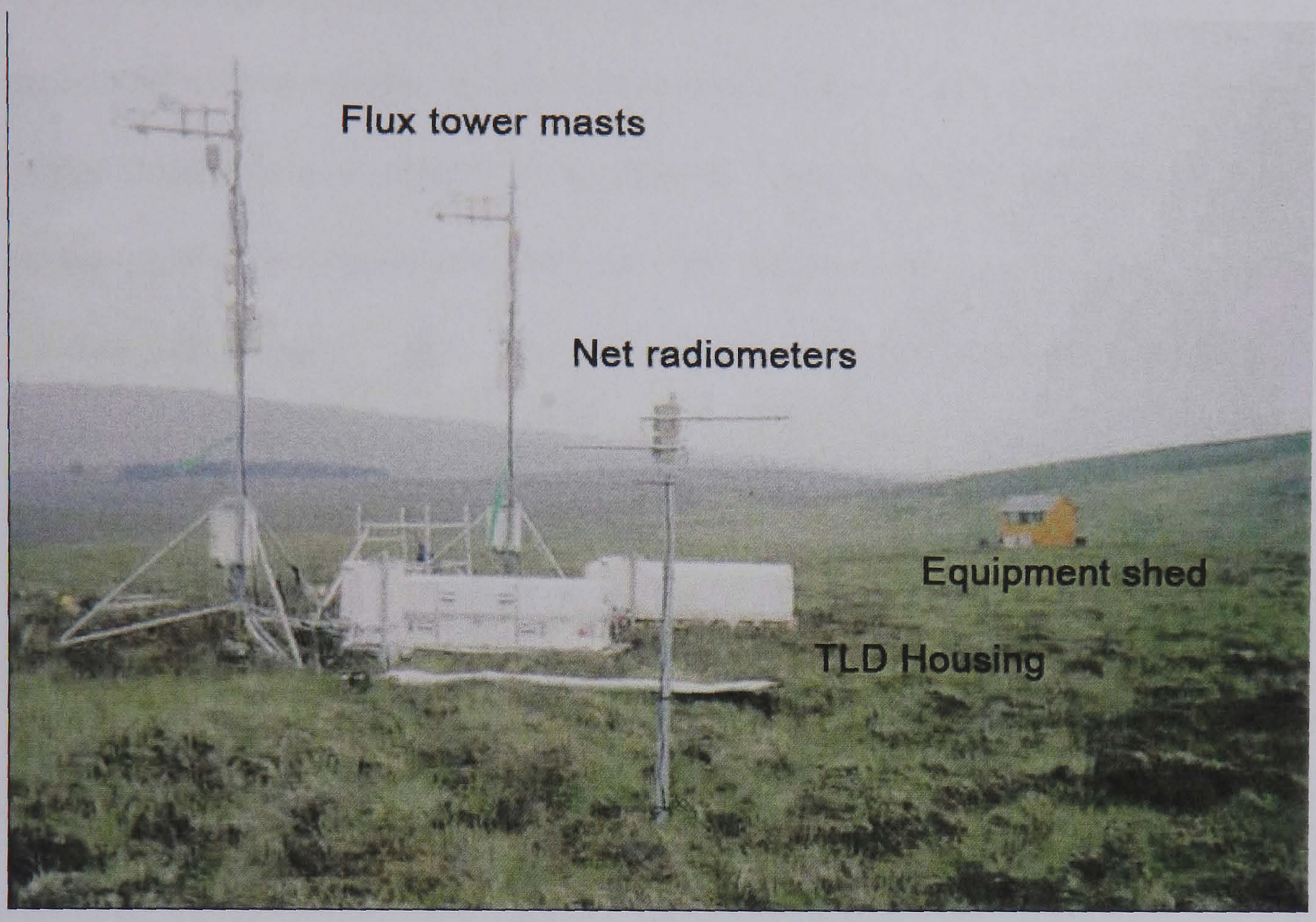

Figure 6.1 Experimental setup at Moor house

Two flux towers were installed by Campbell Scientific US at the Moor house field site. As the field site is about eight miles from the nearest mains electricity supply, a natural gas generator, battery bank, and an array of solar panels were all used to provide power to the flux tower. All the power was regulated by a power inverter (TRACE^{tm} SW Series Inverter/Chargers, XANTREX). This provided continuous power with, in theory, an uninterruptible power supply. The main power was supplied from a set of six large lead acid batteries, when the battery voltage was lowered to below 22 volts, the inverter automatically started the generator, to supply the power and to charge the batteries. Two of the solar panels were wired to a small gel cell battery positioned at the based of the

flux tower masts. These small gel cell batteries provided the power for the data loggers (CR5000 Campbell Scientific), the open path IRGA, sonic anemometer, relative humidity probe, soil moisture probe, and sensible heat flux plates. The solar panels also provided power if there was a problem at the inverter, and the generator failed to start, or the power supply was interrupted. The gel cell batteries were also charged by using the inverter and the battery bank. This was achieved by running a mains power leads from the inverter to the mast (Approximately 50 meters). The mains power cables were run into two power enclosure boxes which housed a power strip and the battery chargers for the gel cell batteries. The power strips had four plug sockets. Two of which were used by the Trace Gas Analyser units, one to power the laser and the other to power the heat and fan.

A Tunable diode laser (TDL) was used to sample the CH_4 concentration in a continuous sample of gas from intake valves (See Figure 6.1) positioned at a height of 3.5 meters on the flux tower masts. An air sample was drawn into the sample tubes by a 1 kilowatt pump positioned 50 meters from the flux towers. These two pumps (One for each mast), were supplied by the generator and batteries. Large pumps were needed to draw down the pressure in the sample tube to about 50 millibar, and to draw the air sample into the sample tube, and this was done from 50 meters away to ensure that there would be no interference from the pumps to either the analogue or digital signals running between the shed and the mast. Cycles in the pump can also affect the laser and produce 'unexplained' cycles in the methane data. Once in the sample tubes the air was passed into a drier to remove the water vapour from the sample. This was done by an osmotic

process. The sample was split into a series of small osmotic tubes over which dry air was passed over the outside and the 'wet' sample air was passed through the small tubes. To prevent the need to have a separate dry air supply, a small proportion of the dried air from the sample air was split off and re-circulated and used as the dry air. The dry air used to dry the sample air was then pumped to waste and expelled into the atmosphere near the shed. The now dry sample air is now passed into the sample tube housed within the TLD box (Figure 6.2).

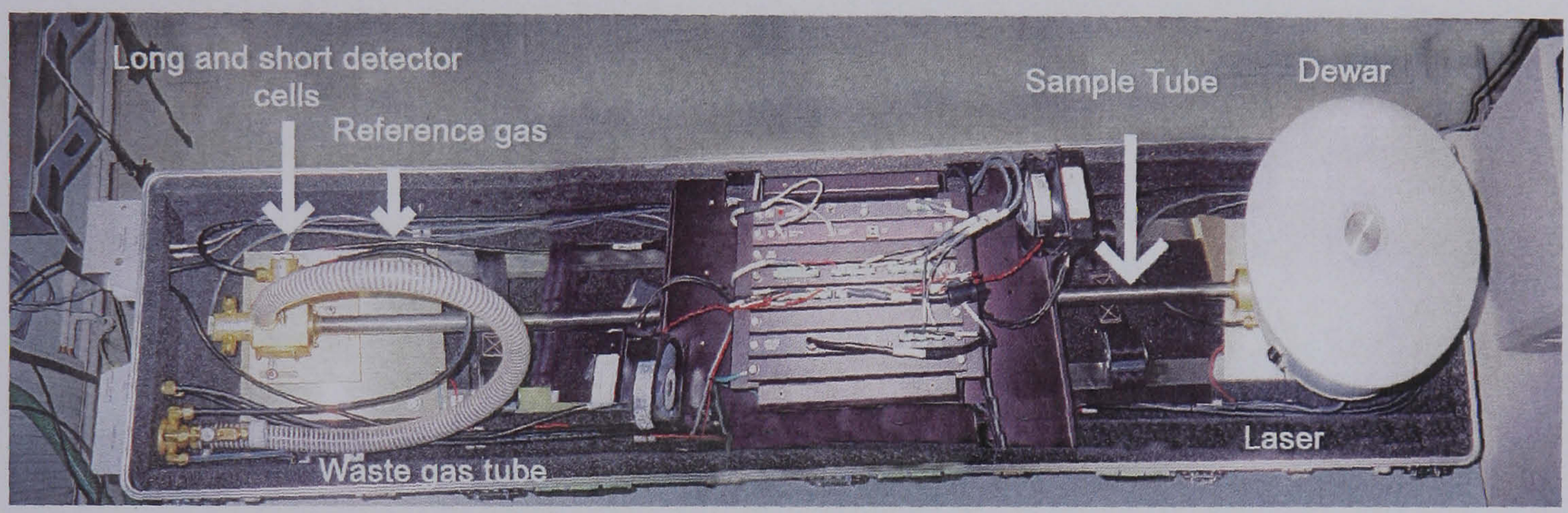

Figure 6.2 Internal picture of a tunable diode laser complete with liquid nitrogen dewar

The picture (Figure 6.2) consists of a stainless steel sample tube about 1.5 metres in length. At one end of this tube is a small window, and at the other end are two detectors labelled the long and short detector cells. In front of the small window is a lead-salt tunable diode laser that operates between 80 and 140 Kelvin. To achieve this extremely cold temperature a Dewar (TGA 100 LN2 Laser Dewar) is mounted above the laser this Dewar holds 10.4 litres of liquid Nitrogen. The laser is cooled using the liquid nitrogen and the exact temperature is controlled by varying the current to the laser. The laser produces a linear wavelength scan centred on a selected absorption line of the trace gas.

The laser is directed into the sample cell and the amount of methane in the sample cell will absorb the radiation proportional to the amount of methane in the sample cell. The beam is then split by a diffraction grating so some of the energy from the beam is directed into the short reference cell, and most of the beam is directed into the long reference cell. In each of these cells there is a detector which provides a spectral shape of the absorption line. Into the short reference cell a speciality reference gas (Supplied by BOC) flows. This reference gas provides a template for the spectral shape of the absorption line, allowing the concentration to be derived independent of the temperature or pressure of the sample gas or the spectral positions of the scan samples. This signal is then outputted via a fibre optic cable to the two PC's where the results can be viewed in real time. These PC's are interactive, and can be used to control the laser temperature, current, as well as other parameters. The PC's will store the 10 hertz data which is the raw data coming from the TDL's at a frequency of 10 times a second. This data, once processed, is outputted from the PC's back to the data loggers on the mast via an analogue output signal.

6.3.3. Climatic measurements

As well as measuring CH_4 and CO_2 the flux tower masts are measuring a host of other environmental variables. Firstly, there are a series of water content reflectometers. These are designed to measure the volumetric moisture content of soils or other porous media (CS616-L, Campbell Scientific US, Utah, Logan). The water content information is derived from the probes sensitivity to the dielectric constant of the medium

surrounding the probe rods. At the field site four water content reflectometers were installed, two for each flux tower. Another probe type used is a temperature and relative humidity probe (CS215, Campbell Scientific US, Utah, Logan). At the field site there are two of these probes, one mounted at each mast. These probes measure the air temperature and the amount of water vapour in the air. This probe is mounted at approximately 3.5 meters above the ground and is enclosed within a radiation shield. Another probe located at the same locations as the water content reflectometers are heat flux plates (HFP01SC, Campbell Scientific US, Utah, Logan). These probes are designed to measure the heat that flows through the object into which it is incorporated. The actual sensor is a thermopile, which measures the differential temperature across the plastic body. The measurement of heat flux through soils is used to determine evaporation of water and thus determine the latent heat flux. Besides the heat flux data, the estimation of evaporation also requires data on solar radiation (NR Lite, Campbell Scientific US, Utah, Logan), wind speed and direction (CSAT-3, Campbell Scientific US, Utah, Logan) and temperature (CS215). Because these other parameters are required to measure evaporation, an NR-lite Net Radiometer has been installed. This is a high output thermopile sensor that measures the algebraic sum of incoming and outgoing all-wave radiation, which consist of both short wave and long wave components (See Figure 6.1). Incoming radiation consists of direct and diffuse radiation plus long wave irradiance from the sky. Outgoing radiation consists of reflected solar radiation plus the terrestrial long wave component. These two probes comprise two of the data sets required to measure evaporation, the last component is the wind speed, and in this case the direction as well. To measure wind speed and direction a sonic anemometer was used. This is a three

dimensional sonic anemometer (See Figure 6.3). It measures the wind speed by analysing the speed of sound in air on three non-orthogonal axes, and the turbulent fluctuations of horizontal, split into x and y components and vertical wind, defined as the z component of air.

Figure 6.3 Campbell Scientific experimental setup, Utah.

6.4. Experimental design

6.4.4. Sampling (frequency and accuracy)

Flux towers provide a unique opportunity to measure CO_2 fluxes continuously over a long period of time with very little human intervention. Flux towers will sample CH_4 and

CO_2 fluxes at a rate of 10 Hz, this measurement period is much faster than the maximum rate of change of either of these fluxes. CO_2 measurements will be on a continuous basis using solar panels to power the open path IRGA and the Campbell scientific logger (CR5000) (See Figure 6.3).

The location of the flux towers has to take into account the predominant wind direction from the field site. This was pre-measured by continuous data from CEH Lancaster, going back many years, and established that there are two dominant wind directions almost due East (EESE) and close to due West (WWNW). This led to the sighting of the rest of the ancillary equipment in the least predominant wind direction, and 50 meters from the flux towers. This is because the generator, when running, produces a large amount of CO_2, which will obviously affect the CO_2 flux results. This is not the only problem because the large pumps that are used to draw down the pressure on the sample tubes on the tunable laser diodes produces enough of a magnetic field to interfere with the results from the flux tower (See Figure 6.1).

The calculation of CO_2 flux data is done by using the 10Hz data from the raw data files and using a measure of the covariance of the vertical upward motion of the wind and the instantaneous measurement of CO_2 concentration (see the equations in appendix 3).

This value is then corrected using the Webb Pearman Leuning correction (Webb et al., 1980), which is based on a correction using sensible and latent heat flux, which involves constants derived by Webb Pearman and Leuning, the density of air, mean CO_2

concentration, temperature, and relative humidity (See Appendix 3). This data analysis then should provide a continuous monitoring of CO_2 flux. This however is not the case as there are some design draw backs with the flux towers. The first and probably the most important is the design of the 3D sonic anemometer, which measures the speed of sound through air and from this calculates wind speed and direction in each of the three components x, y, z. Covering each of the ends of the three pronged analyser are wicking covers which are designed to prevent moisture and precipitation from affecting the readings collected, this is however this design is not perfect, and proportions of the data will be lost during any type of precipitation event, and the flux tower will not collect accurate readings again until the wick has dried out. The problem is compounded without the wick as large water droplets will collect on the end of the sensor dispersing a proportion of the ultrasonic signal giving false wind speed values. This problem can be corrected for by the data logger as the data logger will record the number of errors that it has encountered and then will discount these values from the data processing, which then has problems with there not being enough samples to obtain an accurate measure of CO_2 flux. The flux tower records 18000 samples every 30 minutes, if there are more than 3000 errors in a 30 minute sample then the 30 minute flux measurement was discarded. If the flux towers are not very accurate during rainfall periods, this is a problem because the field site receives over 2 meters of rain a year, with 360 rainfall events during the year. This could seriously affect the quality if the data if accurate fluxes can not be obtain during rainfall periods.

Another limitation of the flux towers are the constants used in the processing software.

These constants are calculated for different field sites to the one which is being measured in this project. The constants used in this project have been provided by Campbell Scientific US and there are user interfaces which allow these constants to be changed and reinstalled onto the logger and the past data files can be reprocessed to include these new variables to ensure continuity of the data set.

6.5. Analysis

Multiple linear regression will be used to determine the significant variables contributing to the flux of CO_2 from the peat surface. This will also allow all the significant variables to be modelled in relation to literature equations. See chapter 2 section 2.3.5 for details on multiple linear regression analysis.

6.6. Results

The flux tower was run between October 2005 and April 2006. Useable readings were collected between 18th of November 2005 and 6th of February 2006 due to technical difficulties. The results measured by the flux tower are compared to the closed chamber CO_2 fluxes measured at the Hexhamshire Common field site, and it is noted that the Hexhamshire Common field site is approximately 18km from the Moor house field site, and therefore a direct comparison cannot be drawn.

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Diurnal cycles of CO_2 fluxes will be affected by: changes in air temperature, which will

affect the soil temperature; and changes in light levels, affecting the amount of CO_2 taken up by the plants. A plot of average half hourly fluxes over time should show these changes in daily fluxes (Figure 6.4).

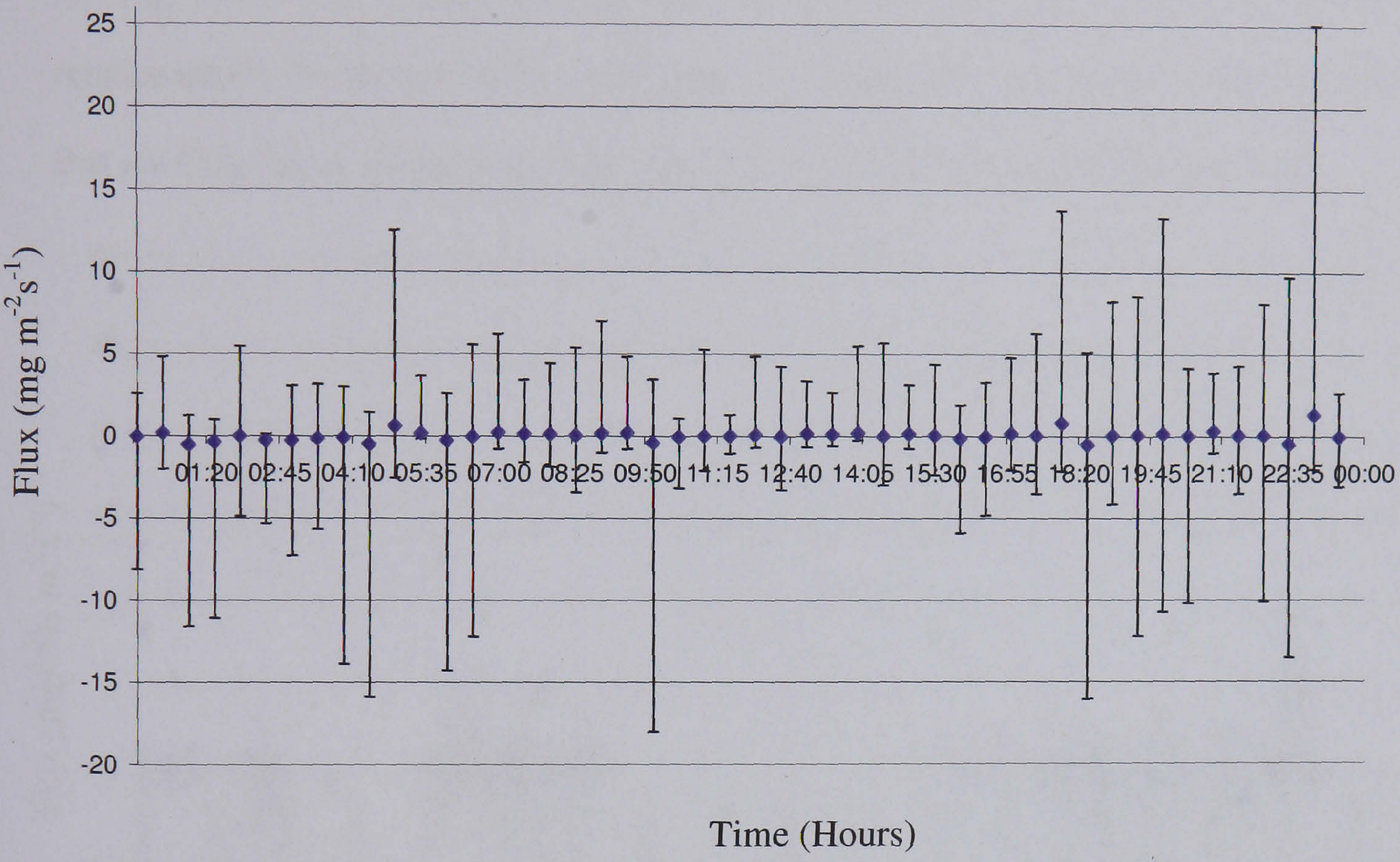

Figure 6.4 Average flux for each 30 minute flux measurement made over the measurement period, plotted over a 24 hour period with maximum and minimum flux within the measurement period as error bar values

As can be seen from the graph (Figure 6.4), there are no obvious diurnal fluxes of CO_2, and the average flux for this time period is approximately zero. A reason for no diurnal fluxes could be that the time period over which the samples were measured, which was during the coldest part of the year, when the CO_2 fluxes would have been low, and the plants were in a state of reduced productivity called senescence. A simple multiple linear regression of CO_2 flux against the time of day shows that there is a statistically significant relationship ($P = 0.023$, $n = 1919$, and $R^2 = 0.3\%$) between CO_2 flux and the

time of day, but does not account for a large proportion of the variation within the flux measurements.

Having found only a slight relationship between flux and time of the day, the next relationship is the change in flux over time. A simple plot of CO_2 flux over time shows that the CO_2 fluxes change over time but with no discernable pattern (Figure 6.5):-

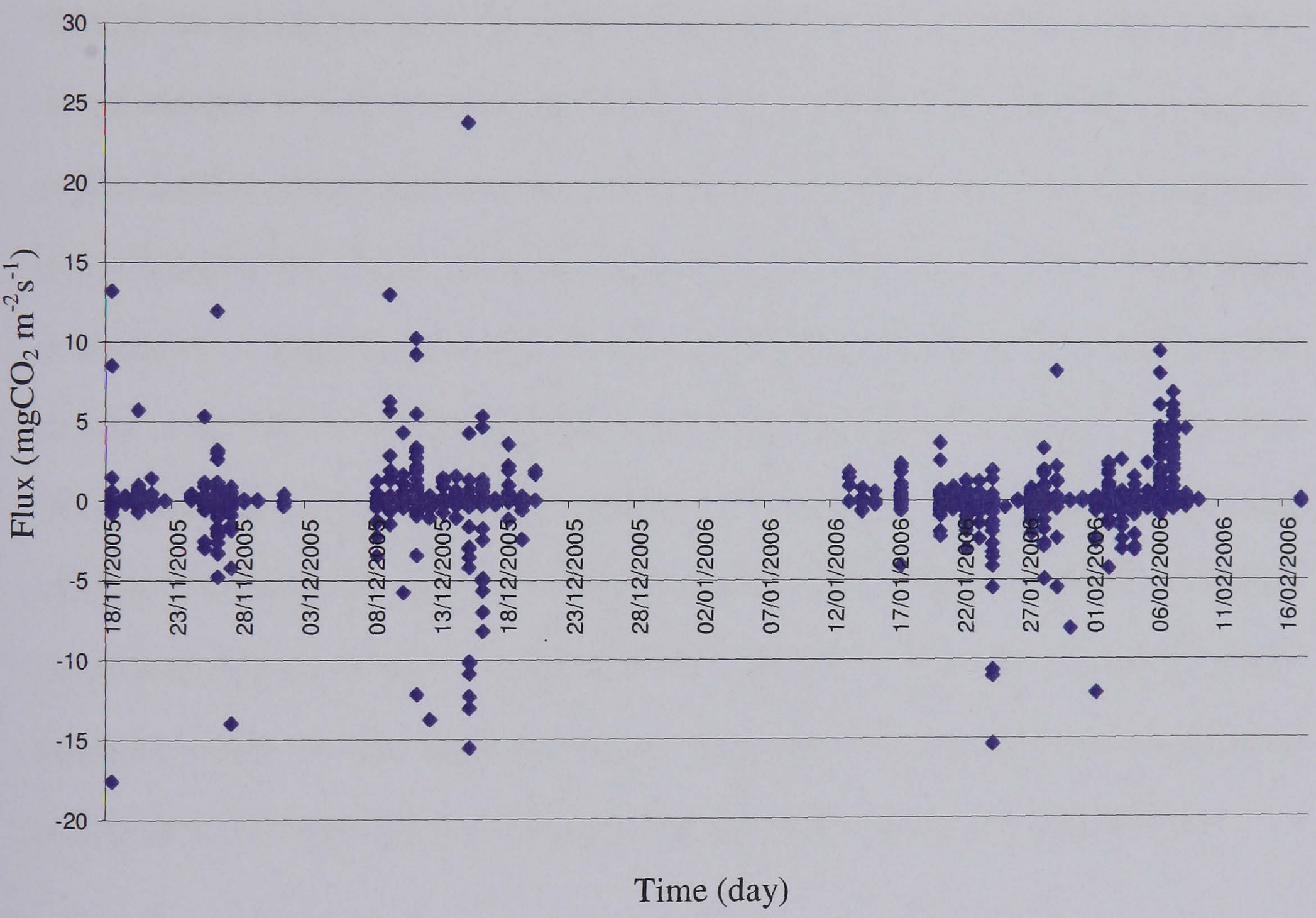

Figure 6.5 CO_2 flux over time

As can be seen from Figure 6.5 there is little systematic change in CO_2 flux over time. The maximum CO_2 flux from the peat surface during this measurement period was 23.8 mg $m^{-2}s^{-1}$, and the maximum uptake was -27.5 mgCO_2 $m^{-2}s^{-1}$ where CO_2 release from the peat surface is positive and uptake of CO_2 is negative. When converted into the same

units as used in chapter 2, these values become; 85.6 gCO_2 $m^{-2}h^{-1}$ and -98.9 gCO_2 $m^{-2}h^{-1}$. When compared to the results collected in chapter 2, section 2.4.6, the maximum CO_2 release was 0.32 gCO_2 $m^{-2}h^{-1}$, whilst the maximum CO_2 uptake was -0.28 gCO_2 $m^{-2}h^{-1}$. The average flux for the flux tower time period is 0.020 $mgCO_2$ $m^{-2}s^{-1}$, which when the units are converted to the units used in chapter 2, is 0.071 gCO_2 $m^{-2}h^{-1}$. Which when compared to the average net flux measurement of -0.16 gCO_2 $m^{-2}h^{-1}$ from the closed chamber measurements shows that the average net CO_2 flux is a larger sink from the closed chamber system than the flux tower. The probable reason for this is that the closed chamber system measured the net fluxes over an entire year, whilst the flux tower only measured the fluxes between November and February, a time of low plant productivity. Comparing the closed chamber CO_2 flux measurements from the same time of year as the flux tower measurements were made (November to February) shows that the maximum CO_2 release was 0.220 gCO_2 $m^{-2}h^{-1}$, the maximum CO_2 uptake was -0.08 gCO_2 $m^{-2}h^{-1}$, and the average was 0.031 gCO_2 $m^{-2}h^{-1}$. These flux measurements (net and gross) from the closed chamber method shows that the measurements made by the closed chamber system (net and night time fluxes, interpreted as gross flux) are much lower during the same measurement period as the net flux readings made by the flux tower.

Analysing the results for the significant variables at the 95% confidence interval from the possible significant variables; Panel temperature (A temperature measure not used in the eddy covariance calculation), wind direction (Compass), wind direction (CSAT), volumetric soil water content (%) x 2 probes, soil temperature x 2 probes, net radiation – observed and corrected. Where, panel temperature is an internal loggerbox temperature

probe not used in the calculation of CO_2 flux, wind direction (compass) is the direction the wind has come from, and is based on standard compass coordinate system, corrected for magnetic variation, with North being 0 and 360 degrees. Wind direction (CSAT), is the wind direction but uses a different coordinate system to a standard compass with the measurement area being divided into four quadrants with the flux tower being the origin at 0,0 where 0,∞ is the averaged predominate wind direction. Volumetric soil water content (%) is the amount of water in the soil as a percentage of the total soil, in this experiment there were two volumetric soil water content probes, there are also two soil temperature probes. Net radiation is the difference between the incoming short wave radiation from the sun, and the amount of long wave radiation from the peat surface. This figure can either be positive or negative depending on the dominate radiation source being the sun or the earth respectively. Logged values of soil temperature (Kelvin) and volumetric soil water content where also used in the regression analysis to test for none linear relationships with the CO_2 flux values. The significant variable from the multiple linear regression was the soil temperature probes of which both probed were significant ($n = 1030$, $P = 0.267$, $R^2 = 1.1\%$), however overall the multiple linear regression was insignificant. Removing the net radiation component from the regression analysis gave the following significant results (Table 6.1)

Variable	P (n= 1378)
Soil temperature probe 1	0.002
Soil temperature probe 2	0.019
LOG Soil temperature probe 1	0.004

LOG Soil temperature probe 2	0.022
LOG average soil temperature	0.010

Table 6.1 Multiple linear regression of flux tower data

As can be seen from Table 6.1 removing the net radiation regression term increases the overall R^2 from 1.1% to 6.2%, and more significant is that the overall the regression becomes significant from P = 0.267 to P = 0.000. The regression equation for Table 6.1 cancels the soil temperature probes. When an average and a log of each soil temperature probe was regressed against flux no significance was found (n = 1378, average soil temperature P = 0.847, log of average soil temperature P = 0.852, R^2 = 0.9%).

The best model so far from Chapter 2, section 2.4.5.3, is a combination of the Lloyd and Taylor equation (Chapter 2 equation 2.vi) and the Bubier equation (Chapter 2 equation 2.viii). The data from the flux tower was sorted for respiration data, which was assumed to be at night between the hours of 11:00pm and 3:00am which, considering the time of the year, is not unreasonable. The respiration data was then predicted using the Lloyd and Taylor equation. This predicted data was then regressed against the actual respiration data from the Moor house site. As there were two soil temperature probes three separate predictions of respiration were calculated using; an average of the two soil probe temperatures and each individual soil temperature probe. In all the regression analyses, there was no relationship significant or otherwise between the predicted soil respiration values and the actual respiration values measured by the flux tower (Soil temperature probe I P=0.537, n=337, R^2=0.1%, Soil temperature probe II P=0.876, n=337, R^2=0.0, Average soil temperature P=0.696, n=337, R^2=0.0).

6.6.5. Error

When analysing this large amount of data, inevitably errors will occur. The largest error in eddy covariance is instrument error. The CR5000 datalogger records the internal flagged error from an instrument. These flagged errors from the instruments are automatically excluded from the flux calculation. The datalogger excludes flagged data, and will reprocess the data without these individual measures. This should exclude any anomalous data. From the above results it can be seen that the largest recorded flux is 23.77 mg $m^{-2}s^{-1}$, and the smallest flux, or greatest uptake is -17.60 mg $m^{-2}s^{-1}$. The largest flux, 23.77 mg $m^{-2}s^{-1}$ had a large number of errors, 1684 error flags and indeed several half hourly flux measurements either side of this flux reading also had a number of error messages. Calculating the CO_2 flux by hand from the raw data file showed that all the flagged errors have been excluded from the flux calculation and that there were no anomalous readings that had not been excluded by the program. Excluding the 30 minute data reading if there were any flagged errors and recalculating the maximum carbon release showed that the greatest carbon release, that has no errors in a 30 minute data set, was 13.17 mg $m^{-2}s^{-1}$. The greatest uptake of carbon results (-17.60 mg $m^{-2}s^{-1}$) had no flagged error messages and an analysis of the raw data file showed that there was no anomalous measurements that the data logger did not flag.

6.7. Discussion

The results presented here are compared to the results collected in chapter 2, although the Hexhamshire Common field site is geographically distant from the Moorhouse field site, the vegetation type, altitude, and climate are similar enough to allow an overall comparison of CO_2 flux, in preference to a comparison of an upland peat from the literature. This allowed a more accurate comparison because different results such as the time of day, when the measurement were taken, the environmental variables at the time can all be included, whilst a literature comparison often excluded these types of details when reporting results. To allow a more detail comparison of CO_2 fluxes from a closed chamber and flux tower would need both a flux tower measuring CO_2 fluxes at a 10Hz frequency, and a series of closed chamber measurements within the footprint of the flux tower. A series of readings taken during dry periods throughout day light hours would be needed to measure net productivity during the day. Combined with these net productivity measurements, a series of respiration measurements taken during dry periods, and again within the footprint of the flux tower, during the night would complete the measurements needed to allow a direct comparison between the closed chamber and flux tower method of collecting CO_2 flux measurements.

One of the main differences in the results between the flux tower and the closed chamber method is that overall the fluxes are of the same order of magnitude, but the maximum and minimum fluxes differ greatly especially as the flux tower measurements were collected during the coldest time of the year, and theoretically the lowest fluxes of CO_2.

When compared to closed chamber flux measurements made during the same time of year as the flux tower measurements, it was found that the flux tower again, had higher average flux measurements and higher maximum and minimum flux measurements. The implication of this could be that the flux measurements taken with the closed chamber system are not measuring the full range of flux values being release by the peat, as is being measured by the flux tower thus underestimating the total fluxes from the Hexhamshire Common site.

From the results section no relationship was found between the time of day and CO_2 flux suggesting that there were no diurnal cycles of CO_2. The most likely reason why this hypothesised relationship was not seen in this data set is due to the time of year. The flux readings were taken at the coldest time of year, when the soil temperatures were at their lowest and thus the soil respiration was at its lowest if the relationship found in chapter 2 fluxes between the fluxes and soil temperature holds for this field site. The plants at the field site will also be at their lowest production levels as both the light levels and temperature were at there lowest. The implications of not having found a diurnal relationship to the flux values is this is that no relationship can be applied to the closed chamber results thus making the mathematical corrections suggested by Bubier (Bubier *et al.*, 1998) and Lloyd and Taylor (Lloyd *et al.*, 1994) to predicted gross and net fluxes from soil temperature and PAR values the best estimates of the net and gross, based on a 15 minute data set.

The maximum and minimum measurements from the flux tower, when compared to the

maximum and minimum flux measurements from the closed chamber method, are two orders of magnitude larger. This is important because the flux tower readings were taken at the coldest time of the year, when the flux measurements would be expected to be low, compared to the CO_2 flux readings taken throughout the year using the closed chamber method when the CO_2 fluxes would be expected to be much higher. When the maximum CO_2 release from the closed chamber flux measurements, taken during the same respective winter months as the measurements made by the flux tower, are compared to the maximum CO_2 release from the closed chamber readings taken in summer, they are 30.7% smaller than the readings taken in the summer. The implication of this is that the flux tower readings could potentially be 30.7% larger than the measurements reported here making the maximum CO_2 release for the flux tower 111.2 $gCO_2\ m^{-2}h^{-1}$. More dramatically the difference between the total amount of CO_2 taken up by the closed chamber method during winter is only 27.8% of the maximum summer uptake. This could mean that the flux tower could have a maximum uptake of -335.5 $gCO_2\ m^{-2}h^{-1}$. This could mean that the Moor House site could be a much large sink than previously thought. These are only maximum release and uptake figures, a more representative figure is the average release and uptake for the flux tower and the closed chamber results taken at the same time of year, and the difference between the average results from the closed chamber winter results and the total average CO_2 flux for a year for the closed chamber results. The gross closed chamber results measured during winter had an average value of 0.031 $gCO_2\ m^{-2}h^{-1}$ and whilst the total average gross readings for the year was 0.069 $gCO_2\ m^{-2}h^{-1}$ showing that the average gross CO_2 release had a value of 45.3% of the total average CO_2 release. The same gross average from the flux tower

measurements has a value of -0.260 gCO_2 $m^{-2}h^{-1}$ this value 54.7% larger gives a value of 0.22 gCO_2 $m^{-2}h^{-1}$ assuming that the soil respiration values become 54.7% more positive, i.e. peat will release more CO_2 during summer. Again, these values show that the flux tower has much greater fluxes compared to the uptake and release fluxes from the closed chamber experiment.

The results collected have to be viewed carefully with respect to the errors. There are seven different types of error or flags that the logger can record, there are three errors associated with the CSAT sonic anemometer, there are individual flag warnings for the H_2O, CO_2, and the temperature systems. Each of these errors leads to an inaccurate estimation of the flux from the site.

From the results section is can be seen that there was no relationship between the best fit model from chapter 2, section 2.4.5.3 Lloyd and Taylor model and the fluxes measured by the flux tower. However, from the regression analysis (Table 6.1) is can be seen that soil temperature is significant. The main problem with this regression is that in the regression equation (Equation 6.xxxviii) the relationship between the two soil probes and the flux measurements is that they have two different relationships. The first soil temperature probe has a positive relationship to the measured flux and the second soil probe has a negative relationship. This would suggest that although the relationship between soil temperature and measured flux is significant, there is not enough of a temperature range to establish a good relationship between soil temperature and flux. Another reason could be that the R_{10} value used to predict the flux at the Moor house site

was taken from an average R_{10} value from the Hexhamshire Common site, and as discussed in chapter 2 section 2.6, an R_{10} value is very changeable depending upon the vegetation within a measurement collar. Therefore, the R_{10} value used in the Lloyd and Taylor equation to predict the respiration from the Moor house site may not be representative of vegetation within the footprint area measured by the flux tower even thought the Hexhamshire Common field site were classified according to the National Vegetation Classification as having the same vegetation type. An R_{10} value was attempted to be calculated based on the fluxes measured by the flux tower using an iterative solving solution, however there was no improvement on the R_{10} value from the Hexhamshire Common R_{10} value. Another reason could be that the maximum soil temperature during that measurement period was only 4.45 ^{0}C and the minimum soil temperature was 0.58^{0}C whilst the definition of an R_{10} value is the respiration value at 10^{0}C, so perhaps there was not a large enough temperature range to accurately define an R_{10} value.

6.8. Further experimentation and problems with the site set up

The main problem with the data collected in this study is the time frame. All of the data was collected during the coldest time of the year when the fluxes would be expected to be at there lowest. This was not intentional, and the flux tower was set during the summer months of 2005. There were lots of initial set up problems, as can be seen from the site

description. The flux tower was set up to measure CO_2 and CH_4 data continuously, however this was not possible as the power inverter was not sensitive enough in its power regulation and would trip the PC's every time it started the generator. This was supported by the fact that the draw down pressure on the pumps fluctuated when the generator was started. Another problem was transporting the liquid nitrogen to the Dewar. Nitrogen can only be transported in a vented Dewar, and up to half of the nitrogen was lost in transport, and a further third was lost in pouring the nitrogen into the Dewar, this increased if there was any wind. A further problem was cooling the Dewars on the TDL. The Dewars held 10.4 litres of nitrogen but required over 30 litres to cool the dewars from atmospheric temperature and fill them with nitrogen. Another problem in the setup was the supply of natural gas for the generator. During the summer there was a small track which ran close to the ancillary site housing the generator, pumps, PC's etc. to which a small Luton van could be driven up, however during winter this track was unsuitable for vehicle use, and the gas had to be carried from further away, and the empty bottles brought down from the site. These problems led to the CH_4 side of the project to be abandoned in favour of CO_2 measurements as continuous data could not be collected for more than 15 hours for CH_4. The CO_2 data was then collected on a more regular basis, with the main problem still being power for the data logger. This was solved by wiring two 65 Watt solar panels into the batteries at the base of the tower. This still did not provide enough power to maintain a continuous charge on the batteries and they had to be changed every week and charged in the lab. This system worked well until a faulty transistor caused the system to fail and had to be sent back to the manufacturer for repair.

6.9. Conclusions

In conclusion, it can be said that the fluxes measured from a flux tower have a much greater magnitude of CO_2 flux than the measurements of flux made with a closed chamber system. This is especially significant if the time of year is considered as the closed chamber measurements were made over the time course of a year whereas the flux tower measured fluxes over a three month period and during the coldest time of the year.

From the results, it can be seen that there is no relationship between the time of day and the flux magnitude. This is significant showing that there are no diurnal cycles during this time of year, and the changes in flux are more related to changes in soil temperature. It was also shown in the results that season was not an important factor in either changes or predicting CO_2 flux for the site.

7. Conclusions

7.1. Introduction

This thesis has examined the complex and diverse nature of gaseous and dissolved CO_2 and gaseous CH_4 released from drained upland peat, and attempted to model them with respect to environmental variables and literature equations and attempted to modify these equations in an attempt to improve the understanding of CO_2 fluxes from upland peat.

7.2. Review of the objectives from this thesis

- Chapter 2, aimed to determine the effects of water table restoration and seasonal variations on CO_2 and CH_4 fluxes. The same chapter also aimed to determine whether season or treatment accounted for most of the variation in CO_2 fluxes. From these results, an annual carbon budget was completed for the gaseous carbon fluxes.
- Chapter 3, aimed to determine the dissolved gaseous concentration of CO_2, and combine these flux results with the gaseous fluxes from chapter 2, to give an overall gaseous and dissolved carbon budget for the Hexhamshire Common field site. The controls affecting the concentration of CO_2 were established, and whether the sources of dissolved CO_2 were mainly from geological or peat-based

sources. It was also hypothesised that there is a constant amount of CO_2 produced, where different driver variables determine whether CO_2 was released gaseously or dissolved into the drainage system.

- Chapter 4, was a climate change experiment, and aimed to determine the effects of; increased temperature, and changing water table depths, on net, gross, and primary productivity CO_2 fluxes. This chapter also aimed to establish whether the CO_2 fluxes measured from the peat cores were comparable with the CO_2 fluxes from the Hexhamshire Common field site with respect to changing temperature and water table depth.
- Chapter 5, aimed to establish the lowest level of monitoring that still gave a good estimate of the carbon budgets for the field site. From these estimates of the carbon budgets, whether the Hexhamshire Common field site was still a sink of carbon or had become a source of carbon could to be established.
- Chapter 6, aimed to quantify the CO_2 fluxes from an upland peat using an eddy covariance, and whether the fluxes were comparable to the fluxes measured using a closed chamber IRGA method. From the flux tower results diurnal fluxes of CO_2 could be established and a correction applied to closed chamber IRGA methods incorporating a modified diurnal cycle based on the flux tower measurements and intensively measurements of soil temperature and PAR.

7.3. Findings and conclusions

7.3.1. Gaseous carbon fluxes

Chapter 2, studied fluxes of CO_2 and CH_4 from an upland peat on a spatial and temporal scale. Combined with these measures of CO_2 and CH_4 fluxes, a suite of environmental measurements were taken at high resolution time periods. From the CO_2 and CH_4 flux measurements, and using multiple linear regression analysis, it was found that there was no relationship between CO_2 and CH_4 and water table depth.

An objective in chapter 2 was to determine whether season or treatment accounted for a greater proportion of the variation. That is, whether the flux readings, divided into winter, spring, summer, and autumn measurements, accounted for a greater proportion of the variation within the CO_2 flux measurements when compared to water table depth. From partial correlation coefficient analysis, it was found that season accounted for a greater proportion of the variance within the gross CO_2 flux data than changes in water table depth. For both net and primary productivity CO_2 fluxes it was found that changes in water table depth accounted for a greater proportion of the variance compared to season.

The final objective of chapter 2 was to establish the best estimate of the carbon budget for the field site for both gaseous CO_2 and CH_4 fluxes. Three methods were proposed in calculating CO_2 and CH_4 flux. The first was a simple averaging of the flux measurements and multiplying this number by the number of hours in a year. This gave a carbon budget estimate of 36.7 tC km^{-2} a^{-1}. This estimate of the carbon budget for the

site did not take into account a large proportion of the seasonal variation from the site as most of the flux measurements were taken in winter. Therefore, a better method was proposed which assumed that there was a linear change in CO_2 flux between CO_2 measurements. This estimate of the carbon budget gave values of 17.7 tC km^{-2} a^{-1}. This method of carbon budget estimate allowed a greater proportion of the summer fluxes to be accounted for. Although this method provides a better estimate of CO_2 flux, it does not take into account diurnal variations in CO_2 flux due to changes in soil temperature and PAR, which from multiple linear regression where proved to be the main drivers of CO_2 flux. Therefore, the last proposed estimated of CO_2 budget for the site involved using equations from the literature and data from the intensively measured 15 minute data set of soil temperature and PAR to model the CO_2 flux for this site. It was found that the literature equations that account for the greater proportion of the variance within the data were the equations by Lloyd *et al.*, (1994) and Bubier *et al.*, (2003). This method of predicting the carbon budget is assumed to be the best because diurnal variation is accounted for and if any of the measured values of CO_2 flux are in error this method of calculating the carbon budget will minimise their effects. From this method it was found that the field site was a source of 17.7 tC km^{-1} a^{-1}.

When the results of the carbon budget from this study where compared to literature values it was found that this drained site released much more carbon than a pristine site (e.g. Trumbore *et al.*, 1999; Roehm *et al.*, 2003; Nykanen *et al* 2003). A drained bog which had subsequently had the water table depth restored had a comparable to higher carbon loss when compared to this study although the method of carbon flux was measured using an eddy covariance method (Nieveen *et al.*, 1998).

7.3.2. Dissolved CO_2

Chapter 3, studied the amount of carbon released as excess CO_2 from an intensely drained upland peat by measuring dissolved CO_2 from a blocked grip, an open grip, an old blocked grip and a natural stream. Excess CO_2 in solution was calculated for the field site by using a titration method, and chemical processing procedure proposed by Ringbom, which is a chemically robust method for calculating the excess CO_2 concentration from solution. The total buffering capacity for a solution from a drainage system was measured using a gran alkalinity or acidity method depending on the pH. The excess CO_2 compared to the concentration of CO_2 in the atmosphere, was calculated using a speciation model which required the breakdown of the different dissolved species in the solution. These were found to be calcium, aluminium, and DOC in their various speciated forms. It was concluded from these results that the Hexhamshire Common field site was a small source of between 10.56 and 18.67 gC m^{-2} a^{-1}. It was also concluded that the dissolved CO_2 fluxes were similar to the gaseous CO_2 fluxes from Chapter 2 – gaseous carbon fluxes, with the average dissolved CO_2 flux being 17.667 gC m^{-2} a^{-1} whilst the gaseous CO_2 was 17 .73 gC m^{-2} a^{-1}.

When the two flux values (Gaseous and dissolved) were considered as being produced from a single mechanism from within the peat it was found that the total amount of CO_2 being produced could be better modelled using the equation defined by Lloyd *et al.*, (1994). From this conclusion a link between water table depth and total CO_2 flux was

reconsidered. In predicting R_{10} values from the total CO_2 flux, that is the combined gaseous and dissolved CO_2 flux, it was found that the R_{10} values were proportional to the average water table depth for each collar. This lead to the R_{10} values being linked to the water table depth via a linear equation which improved the amount of variance explained for the gross fluxes by the Lloyd and Taylor equation (Chapter 2, section 2.4.5, equation 2.vi). Therefore, rather than give separate R_{10} values for each collar a single formula is proposed that links all the collars to the amount of CO_2 produced at 10°C and at a water table depth of 10cm. Another conclusion that can be drawn from this linear equation is that there is a contribution from the anaerobic zone to the total CO_2 flux predicted by the intercept value from the linear equation. From the linear equation used to link water table depth to respiration rate at a given temperature the gradient of the equation can be said to be equivalent to the rate of CO_2 production by the soil microbe community. Therefore, the gradient can be used as a simple descriptor of the microbial community of peat. This raises the question; is this gradient value constant between different microbial communities from both peat and other soil environments or is it different. The one other study that has come to the same conclusion that gaseous CO_2 flux R_{10} (not gaseous and dissolved CO_2) is linked to water table depth (Lloyd, 2006), and the figures quoted within the paper were different than the figures found in this study.

The amount of CO_2 in solution was inversely related to the flow in the grips. This is interpreted as contribution of old, soil pore water into the grip system increasing as the contribution of rainfall, or new water, decreased. From statistical analysis of conductivity, flow, average daily rainfall, and treatment (Grip type) were all significant at the 95% confidence interval. These results mean that the amount of CO_2 in solution is

related to the amount of water within the drainage system. As conductivity is significant this means that dissolved CO_2 makes up a large proportion of the total dissolved species in solution. Flow is related to the amount of CO_2 in solution with the greater the flow the more carbon exported as dissolved CO_2, even though concentration of CO_2 in solution is inversely related to concentration. Therefore, the grips or treatments that are allowed to drain freely export more carbon as can be seen from the amount of carbon exported by Hex 2 and Widdybank fell.

7.3.3. Carbon dioxide release from peat cores

A series of deep peat cores were removed from the Hexhamshire Common field site and moved to a warmer drier location to simulate a climate change of approximately 4°C. The water table depth was controlled to simulate normal and drought conditions.

It was concluded that the data collected from the peat cores were visually comparable with the data collect from gaseous CO_2 samples from Hexhamshire Common however upon statistically analysis of the results revealed that the results were not comparable, and therefore peat cores cannot be removed from an upland peat and used to simulate climate change. The data from the peat core temperature range was much greater than the temperature range from Hexhamshire Common, with the average air temperature at Hexhamshire Common being 8.94°C, and the average air temperature over the time period the peat cores were measured was 23.96°C. This is important, in relation to climate change, as the greater the temperature the more CO_2 is released and suggests that

peat CO_2 release does not plateau out above a certain temperature.

It was found that water table was significant in relation to the CO_2 fluxes from the peat core, and it was concluded that the deeper the water table depth the greater the CO_2 `release. In the experiment the water table was decreased and then increased to see if there was a disproportionate increase in the amount of CO_2 release due to a simulated drought relative to the water table at the same depth during the water table reduction. It was concluded that whether the water table was decreasing in depth or increasing in depth did not make a difference to the CO_2 flux.

7.3.4. Calculation of Gaseous and Dissolved Carbon budgets

Chapter 5, took mass load estimation equations from the literature and applied them to both dissolved and gaseous CO_2 flux. Applying export budgets to dissolved CO_2 shows that simple linear extrapolation is not valid for calculating gaseous carbon budgets, these equations also showed how representative a concentration sample is relative to a driving function, such as flow. This was proposed by Littlewood as method A (Littlewood *et al.*, 1998), this equation allowed the instantaneous concentration of dissolved CO_2 to be compared to the instantaneous flow at the instant of sampling to the average flow within a user defined time period. This method reduces the uncertainty within sampling frequency and due abnormal sampling events. Method A also showed that simply assuming that there was a linear change in dissolved CO_2 concentration between

sampling events underestimated the total carbon export for the site, giving an export value for the Hexhamshire Common site of 18.2 KgC a^{-1}, compared to 24.0 KgC a^{-1} estimated by method A.

7.3.5. Eddy Covariance

Chapter 6, described the siteing and establishing of a flux tower, and the basic equations behind eddy covariance. The flux tower sampled both CO_2 and CH_4 however due to power difficulties the most continuous data set was CO_2. The main data processing from raw data to a flux reading uses eddy covariance which is a useful method for measuring long term fluxes over areas much larger than can be measured using a closed chamber method. The main experimental problem with flux towers is taking measurements during any rainfall event when the three dimensional wind speed analysis sensor becomes wet and disperses the ultrasonic sound signal which provides direction and speed of the instantaneous wind and is at the very heart of eddy covariance measurements.

When eddy covariance flux measurements were compared to closed chamber fluxes, taken during the same time of the year from a similar environment, it was shown that the long term averages where similar, however maximum and minimum half-hourly flux readings had a much greater difference. This lead to the conclusion that eddy covariance were much more susceptible to small changes in environmental variables and eddy covariance instrumentation was suspect to a larger range of errors than closed chamber measures but would provide much more information on spatial and temporal CO_2 fluxes than chamber measures ever could.

7.4. Data Limitations

One of the main and most obvious data limitations with this type of study is the time frame over the measurements were made. The more measurements, and the longer the time period over which sample and measurements can be taken the better. One of the main limitations in this study is the use of a closed chamber method. Closed chamber methods are prone to the following problems:-

- Leakages, especially at the chamber collar interface.
- An interaction effect between the chamber and the peat when the chamber is place on the peat due to ebullition.
- The effect of the collar permanently installed in the peat and vegetation.
  Installing the collar involved cutting some of the plant roots. Depending on the siteing of the collar the vegetation either survived, but was reduced in height and quantity or the vegetation died.
- The size of the chamber prevented measuring the carbon fluxes from larger, older heather stands as they could not be physically fitted in the chamber, and if the vegetation in the chamber was too large the volume of the chamber would have been dramatically altered and thus give an over estimation of the carbon fluxes.

With respect to the study of dissolved CO_2, the major limitation is the sampling methods. Water samples were collected in large (1litre) bottles and analysed the same day, but there was several hours between collection and titration, and although the bottles were sealed without any head space, often when the samples were analysed back at the lab,

there were small air bubbles in the bottles. This was removed by refrigerating the samples for a few minutes prior to titration.

7.5. Recommendations for future work

From the results found here it would seem that all the CO_2 produced within the peat is linked to both soil temperature and water table depth. From literature equations (Lloyd *et al.*, 1994) and the improvements suggested here to include dissolved CO_2 and water table depth, further discussion is need to ascertain whether these equations can mathematically describe the microbial production of CO_2. If they can then there is a need to establish whether these microbial communities vary across different peat environments, and indeed different soil communities, potentially linking large areas of research together. Work is also need to establish the link, not only between water table depth but, with soil moisture as well. In this study it was assumed that there was no limitations in CO_2 flux due to soil moisture deficit. During the summer months, water table depths could be as low as 50 cm, with the top few centimetres of the peat being very dry. From studying the residuals of the Lloyd and Taylor equation (Chapter 2, section 2.4.5.3) it can be seen that the equation is a poorer predictor of gross CO_2 flux at high temperatures. This may be interpreted as CO_2 production being limited by soil moisture.

In increasing the predictive power of the models proposed here, specifically to predict the amount of dissolved CO_2 in solution in the drainage system, similar models used to predict unit hydrographs could be used which are based on the amount of rainfall the catchment receives, the time since last rainfall, and the amount of evapotranspiration

from a catchment. It is proposed here that this type of model could be modified, by incorporating the Lloyd and Taylor equation (Lloyd *et al.*, 1994) and the modifications proposed here, to predicted the total amount of CO_2 produced and the amount of CO_2 'washed' from the system during a rainfall event, based on a unit hydrograph prediction.

8. Appendix 1

Activity constants within a river system can be defined by the speed by which different species disassociate within the river system. This can be defined experimentally by dissolving the different species in water and measuring the change in concentration of each species within the sample over time at a certain temperature. If the rate at which the concentrations change is plotted over time and a regression curve fitted to the data, this regression curve can be used to find the disassociation constant at a given temperature. Therefore the constant within each speciation reaction can be defined by measuring the water temperature. This can be done with the equations from the speciation reactions.

8.1. Carbonate Speciation and Analytical Expressions for Temperature Dependence

The disassociation constant for Henry's law is defined as:-

$$K_H = \frac{\lfloor Dissolved\ CO_2 \rfloor}{Gaseous\ CO_2} \qquad \textbf{8.i}$$

The value for K_H has been defined according to water temperature (K) as:-

$$K_H = 10^{\left(108.3865 + 0.01985076 \times Water\ temperature - \frac{6919.53}{Water\ Temperature} - 40.45154 \times (LOG\ Water\ Temperature) + \frac{669365}{Water\ temperature^2}\right)} \qquad \textbf{8.ii}$$

This can be done for the other disassociation equations in the speciation model.

$$K_0 = \frac{\lfloor H_2CO_3 \rfloor^*}{pCO_2} \qquad \lfloor H_2CO_3 \rfloor^* = \lfloor Dissolved\ CO_2 \rfloor + \lfloor H_2CO_3 \rfloor \qquad \textbf{8.iii}$$

$$K_0 = 10^{-\left(13.417-\left(\frac{2299.6}{Water\ Temp\ erature}\right)-(0.01422\times Water\ tem\ perature)\right)}$$

8.iv

Disassociation constant equation of K_0 and disassociation value defined by water temperature for K_0

$$K_1 = \frac{[H^+]\times[HCO_3^-]}{[H_2CO_3]}$$

8.v

$$K_1 = 10^{\left(-356.3094-0.06091964\times Water\ temperature+\frac{21834.37}{Water\ temperature}+126.8339\times(LOG\ Water\ temperature)-\frac{1684915}{Water\ temperature^2}\right)}$$

8.vi

Disassociation constant equation of K_1 and disassociation value defined by water temperature for K_1

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

8.vii

$$K_2 = 10^{\left(-107.8871-(0.03252849\times Water\ temperature)+\left(\frac{5151.79}{Water\ temperature}\right)+(38.92561\times(LOG\ Water\ temperature))-\left(\frac{563713.9}{Water\ Temperature}\right)\right)}$$

8.viii

Disassociation constant equation of K_2 and disassociation value defined by water temperature for K_2

8.2. Calcium Speciation and Analytical Expressions for Temperature dependence

$$K_3 = \frac{[CaHCO_3^+]}{[Ca^{2+}][HCO_3^-]}$$

8.ix

$$K_3 = 10^{(1209.12 + 0.31294 \times \text{Water temperature} - 34765.05 - 478.782 \times (LOG\ \text{Water temperature}))}$$

8.x

Disassociation constant equation of K_3 and disassociation value defined by water temperature for K_3

$$K_4 = \frac{[CaCO_3]}{[Ca^{2+}][CO_3^{2-}]}$$

8.xi

$$K_4 = 10^{-7.0017}$$

8.xii

Disassociation constant equation of K_4 and disassociation value at 298.15K of K_4

$$K_5 = \frac{[CaOH^+]}{[Ca^{2+}][OH^-]}$$

8.xiii

$$K_5 = 10^{-12.85}$$

8.xiv

Disassociation constant equation of K_5 and disassociation value at 298.15K of K_5

$$K_w = [H^+][OH^-]$$

8.xv

$$K_w = 10^{\left(-298.97 + \left(\frac{13323}{Water\ temperature}\right) - 0.05069842 \times (Water\ temperature) + 102.24447 \times (LOG\ \ Water\ temperature) - \frac{1119669}{Water\ temperature^2}\right)}$$

8.xvi

Disassociation constant equation of K_w and disassociation value defined by water temperature for K_w

$$K_7 = [Ca^{2+}][CO_3^{2-}]$$

8.xvii

$$K_7 = 10^{-171.9773 - 0.077993 \times Water\ temperature + \frac{2903.293}{Water\ temperature} + 71.595 \times (LOG\ \ Water\ temperature)}$$

8.xviii

Disassociation constant equation of K_7 and disassociation value defined by water temperature for K_7

8.3. Aluminium Speciation and Analytical Expressions for Temperature dependence

$$K_{1Al} = \frac{[Al(OH)^{2+}]}{[Al^{3+}][OH^-]}$$

8.xix

$$K_{1Al} = 10^{-38.253 - \frac{656.27}{Water\ temperature} + 14.327 \times (LOG\ \ Water\ temperature)}$$

8.xx

Disassociation constant of K_{1Al} and disassociation value defined by water temperature for K_{1Al}

$$K_{2Al} = \frac{[Al(OH)_2^+]}{[Al^{3+}]2[OH^-]}$$

8.xxi

$$K_{2Al} = 10^{88.500-\frac{9391.6}{Water\ temperature}\ 27.121\times(LOG\ Water\ temperature)}$$

8.xxii

Disassociation equation of K_{2Al} and disassociation value defined by water temperature for K_{2Al}

$$K_{3\,Al} = \frac{[Al(OH)_3]}{[Al^{3+}]3[OH^-]}$$

8.xxiii

$$K_{3\,Al} = 10^{226.374-\frac{18247.8}{Water\ temperature}\ 73.597\times(LOG\ Water\ temperature)}$$

8.xxiv

Disassociation equation of K_{3Al} and disassociation value defined by water temperature for K_{3Al}

$$K_{4Al} = \frac{[Al(OH)_4]}{[Al^{3+}]4[OH^-]}$$

8.xxv

$$K_{4Al} = 10^{51.578-\frac{111689}{Water\ temperature}\ 14.865\times(LOG\ Water\ temperature)}$$

8.xxvi

Disassociation equation of K_{4Al} and disassociation value defined by water temperature for K_{3Al}

Having defined the disassociation equations and defining the constant values in relation to temperature these terms need to be combined to define the total speciation of every species within solution. This is the purpose of Appendix 2.

9. Appendix 2 calculating acidity from first principals

Combining the equations from appendix 1 to define the overall buffering capacity of a solution shows that the overall buffering capacity is equal to the sum of all the dissolved species within a solution. Therefore the overall buffering capacity of a solution from upland peat can be defined as:-

$$C^T = \sum DIC\ species + \sum Calcium\ species + \sum Aluminium\ species + \sum Organic\ species \quad \textbf{9.i}$$

So breaking the equation down into its constituent parts the equation becomes:-

$$C^T = ([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]) + ([Ca^{2+}] + [CaCO_3] + [Ca(OH)^+] + [Ca(OH)_2] + [CaHCO_3^+]) + ([Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_3] + [Al(OH)_4]) + ([H_2org] + [Horg^-] + [org^{2-}]) \quad \textbf{9.ii}$$

Having define the overall speciation reaction of the sample, defining every term in the reaction other than the unknown excess CO_2, will mean that there is only one unknown in the speciation reaction, and this can be defined by rearranging the equation to find the excess dissolved CO_2 within the sample. To define the concentration of every species within the water sample the total concentration of each species is measured along with the pH and water temperature. Using the temperature dependant constants from appendix 1 and redefining the concentrations of each species from equations 2 to 14 in there simplest forms will allow the speciation equation to be solved.

Redefining the concentrations in their simplest form was done using Ringbom's theory. To find the concentration of CO_3^{2-}, Ringbom's equation is used to find the missing parts

of the equation relating to activity constants. So:-

$$CO_3^{2-} = \frac{C^T}{\alpha_H} \qquad \textbf{9.iii}$$

To find the concentration of CO_3^{2-} equation 9.iii needs to be redefined with respect to the activity constants as defined by water temperature from appendix 1, and defined by their simplest terms.

9.1. Carbonate speciation

$$K_{H_2CO_3} = \frac{[H_2CO_3]}{[H^+][HCO_3^-]} \qquad \textbf{9.iv}$$

Becomes:-

$$[H_2CO_3] = \frac{[H]^2[CO_3^{2-}]}{K_{H_2CO_3} K_{HCO_3}} \qquad \textbf{9.v}$$

$$K_{HCO_3} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \qquad \textbf{9.vi}$$

Becomes:-

$$[HCO_3^-] = \frac{[H^+][CO_3^{2-}]}{K_{HCO_3^{2-}}} \qquad \textbf{9.vii}$$

$$k_{CO_3^{2-}} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \qquad \textbf{9.viii}$$

Becomes:-

$$[CO_3^{2-}] = \frac{[CO_3^{2-}]}{K_{CO_3^{2-}} K_{HCO_3}}$$

9.ix

9.2. Calcium Speciation

$$k_{CaCO_3} = \frac{[CaCO_3][H^+]}{[Ca^{2+}][HCO_3^-]}$$

9.x

Becomes:-

$$[CaCO_3] = \frac{Ca^T K_{CaCO_3} C^T}{K_{CO_3^{2-}} \alpha_H \alpha_{Ca^{2+}}}$$

9.xi

$$K_{CaHCO_3^+} = \frac{[CaHCO_3]}{[Ca^{2+}][HCO_3]}$$

9.xii

Becomes:-

$$[CaHCO_3] = \frac{Ca^T [H^+] K_{CaHCO_3^+} C^T}{K_{CO_3^{2-}} \alpha_H \alpha_{Ca^{2+}}}$$

9.xiii

$$K_{CaOH^+} = \frac{[CaOH^+][H^+]}{[Ca^{2+}]}$$

9.xiv

Becomes:-

$$[Ca(OH)^+] = \frac{K_{Ca(OH)^+} Ca^T}{\alpha_{Ca^{2+}} [H^+]}$$

9.xv

$$K_{Ca(OH)_2} = \frac{[Ca^{2+}]}{[Ca(OH)_2][H^+]}$$

9.xvi

Becomes:-

$$[Ca(OH)_2] = \frac{Ca^T}{K_{Ca(OH)_2}[H^+]\alpha_{Ca^{2+}}} \qquad \textbf{9.xvii}$$

9.3. Aluminium Speciation

$$K_{Al(OH)^{2+}} = \frac{[Al^{3+}][H^+]}{[Al(OH)^{2+}]} \qquad \textbf{9.xviii}$$

Becomes

$$[Al(OH)^{2+}] = \frac{[Al^{3+}][H^+]}{K_{Al(OH)^{2+}}} \qquad \textbf{9.xix}$$

$$K_{Al(OH)_2^+} = \frac{[Al(OH)^{2+}][H^+]}{[Al(OH)_2^+]} \qquad \textbf{9.xx}$$

Becomes:-

$$[Al(OH)_2^+] = \frac{[Al^{3+}][H^+]^2}{K_{Al(OH)^{2+}} K_{Al(OH)_2}} \qquad \textbf{9.xxi}$$

$$K_{Al(OH)_3} = \frac{[Al(OH)_2^+][H^+]}{[Al(OH)_3]} \qquad \textbf{9.xxii}$$

Becomes:-

$$[Al(OH)_3] = \frac{[Al^{3+}][H^+]^3}{K_{Al(OH)^{2+}} K_{Al(OH)_2^+} K_{Al(OH)_3}} \qquad \textbf{9.xxiii}$$

$$K_{Al(OH)_4}=\frac{[Al(OH)_3][H^+]}{[Al(OH)_4]}$$ **9.xxiv**

Becomes:-

$$[Al(OH)_4]=\frac{[Al^{3+}][H^+]^4}{K_{Al(OH)^{2+}}K_{Al(OH)_2^+}K_{Al(OH)_3}K_{Al(OH)_4}}$$ **9.xxv**

9.4. Organic Speciation

$$K_{Horg^-}=\frac{[org^{2-}][H^+]}{[Horg^-]}$$ **9.xxvi**

Becomes:-

$$[Horg^-]=\frac{[org^{2-}][H^+]}{K_{Horg^-}}$$ **9.xxvii**

$$K_{H_2org}=\frac{[Horg^-][H^+]}{[H_2org]}$$ **9.xxviii**

Becomes:-

$$[H_2org]=\frac{[org^{2-}][H^+]^2}{K_{H_2org}k_{Horg^-}}$$ **9.xxix**

Defining α by dividing equations through by either CO_3^{2-}, Ca^{2+}, Al^{3+}, or org^{2-}, and rearranging the equations so that they are defined in the simplest units. For example:-

$$\alpha_{Ca}=\frac{Ca^T}{Ca^{2+}}$$ **9.xxx**

$$[Ca^T] = [Ca^{2+}] + [CaCO_3] + [CaOH^-] + [Ca(OH)_2] + [CaHCO_3^+] \quad \textbf{9.xxxi}$$

$$\alpha_{Ca} = 1 + \left(\frac{C^T K_{CaCO_3}}{K_{CO_3^{2-}} \alpha_H}\right) + \left(\frac{K_{CaHCO_3^-} C^T [H^+]}{K_{CO_3^{2-}} \alpha_H}\right) + \left(\frac{1}{K_{Ca(OH^-)_2} [H^+]}\right) + \left(\frac{K_{CaOH^+}}{[H^+]}\right) \quad \textbf{9.xxxii}$$

$$\alpha_{Al} = \frac{Al^T}{Al^{3+}} \quad \textbf{9.xxxiii}$$

$$\alpha_H = 1 + \left(\frac{[H^+]}{K_{CO_3^{2-}}}\right) + \left(\frac{[H^+]^2}{K_{CO_3^{2-}} K_{HCO_3}}\right) + \left(\frac{K_{CaCO_3} [Ca^T]}{K_{CO_3^{2-}} \alpha_{Ca}}\right) + \left(\frac{K_{CaHCO_3^-} [H^+][Ca^T]}{K_{CO_3^{2-}} \alpha_{Ca}}\right) \quad \textbf{9.xxxiv}$$

These equations are then all combined into the C^T formula to define the overall speciation concentration.

$$C^T = ([H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]) + ([Ca^{2+}] + [CaCO_3] + [Ca(OH)^+] + [Ca(OH)_2] + [CaHCO_3^+]) +$$
$$([Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_3] + [Al(OH)_4]) + ([H_2org] + [Horg^-] + [org^{2-}]) \quad \textbf{9.xxxv}$$

$$CO_3^{2-} = \frac{C^T}{\alpha_H} \quad \textbf{9.xxxvi}$$

So α_H is equal to:-

$$\alpha_H = 1 + \left(\frac{H^+}{K_2}\right) + \left(\frac{(H^+)^2}{K_2 \times K_1}\right) + \left(\frac{\left(K_{CaCO_3^0} \times Total\ Calcium\ conc.\right)}{K_2 \times \alpha_{Ca}}\right) +$$

$$\left(\frac{\left(K_{Ca(OH)_2^0} \times H^+ \times Total\ Ca\ Conc.\right)}{K_2 \times \alpha_{Ca}}\right) + \left(\frac{\left(K_{Al(OH)^{2+}} \times Total\ Ca\ Conc.\right)}{\alpha_{Ca} \times H^+}\right)$$

$$+ \left(\frac{Total\ Ca\ Conc.}{\left(K_{Ca(OH)_2^0} \times H^+ \times \alpha_{Ca}\right)}\right) + \left(\frac{\left(Total\ Al\ Conc. \times H^+\right)}{K_{Al(OH)_2^+} \times \alpha_{Al}}\right) +$$

$$\left(\frac{\left(Total\ Al\ Conc. \times (H^+)^2\right)}{K_{Al(OH)_2^+} \times K_{Al(OH)^{2+}} \times \alpha_{Al}}\right) + \left(\frac{\left(Total\ Al\ Conc. \times (H^+)^+\right)}{K_{Al(OH)_3^0} \times K_{Al(OH)_2^+} \times K_{Al(OH)^{2+}} \times \alpha_{Al}}\right) +$$

$$\left(\frac{\left(Total\ Al\ conc. \times (H^+)^2\right)}{K_{Al(OH)_4^-} \times K_{Al(OH)_3^0} \times K_{Al(OH)_2^+} \times K_{Al(OH)^{2+}} \times \alpha_{Al}}\right) +$$

$$\left(\frac{\left(Total\ organic\ conc. \times (H^+)^2\right)}{K_{Horg^-} \times K_{H_2org^0} \times \alpha_{org}}\right) + \left(\frac{\left(Total\ organic\ conc. \times H^+\right)}{K_{Horg^-} \times \alpha_{org}}\right) \quad \textbf{9.xxxvii}$$

Appendix 3. Introduction to Eddy Covariance

The theory behind the measurements of gaseous carbon from a field site can be thought of as a point source of CO_2 on a homogeneous surface some distance from the flux tower. The initial concentration of CO_2 at the point source will not be the same as the concentration measured at the flux tower as there are factors such as the distance to the flux tower, the three dimensional wind speed (Ux = Predominant wind direction and speed, Uy = cross wind direction and speed, Uz = upward/downward wind direction and speed), and temperature (K) which will act on the point source gas and diffuse it. The initial point source can be thought to disperse as a plume, with the concentration dispersing upwards, depending on Uz, and the amount of dispersion of the plume dependant upon temperature. This leads to the basic equation based upon Pasquill and Smith (1983) defined by Schmid (2002), see Appendix 2. These equations can also be used to calculate the flux of any gas from nitrogen, methane and sulphur. In this experimental set up both CO_2 and CH_4 will be measured, and the equations applied to both CO_2 and CH_4 with obvious corrections for molecular weight.

Equations from Schmid (2002) which provide an introduction to the equations used in Eddy Covariance are presented below and some of the reasoning behind the equations used.

The basic equation defined by Schmid is based upon theoretical plume dispersion models. This led to the equation 6.i.

$$\eta(r) \int Q_{\eta}(r+r')f(r+r')dr'$$

6. i

Where η is the measurement height at location *r*, *Qη(r+r')* is the distribution of source or sink strength in the surface vegetation volume, and *f(r,r')* is the footprint or transfer function depending on *r*, and on the separation between measurement and forcing , *r'*. The integration is performed over a domain R.

This understanding of how plumes or concentrations of gasses act over different volumes and areas depending upon different climatic processes, leads us into defining carbon fluxes of carbon by using rapid sampling techniques, and computer processing, can be used to define much more accurately the carbon exchanges occurring on a field site than chamber sampling.

These eddy covariance measurements can be visualised as split second measurements of the area immediately upwind from the sample location i.e. the flux tower, and the measurements made are depended upon many different factors. The basic factors measured are; wind speed, temperature, CO_2 concentration, relative humidity, and atmospheric pressure. Using the Webb, Pearman and Leauning (wpl) Correction (Webb *et al.*, 1980), which states that the time rate of change of the mean concentration of CO_2 at a fixed point in space is balanced by the mean horizontal and vertical advection by the mean horizontal and vertical divergence or convergence of the turbulent flux, by molecular diffusion, and any sink or source (Baldocchi et al., 2001), is equal to:-

$$Flux = \overline{(mean\ vertical\ wind\ speed) \times (mean\ air\ density) \times (fraction\ of\ the\ carbon\ density\ in\ air)}$$

6. ii *Where overbar denotes an average*

This equation can be redefined as an energy balance equation where each of the above components can be expressed by the amount of energy required to heat or cool the volume of air (Sensible Heat flux), and the amount of energy required to change the phase of a substance e.g. from a liquid to a gas (Latent Heat Flux), which will give the flux of carbon if the concentration of carbon is know at a point source, ie the concentration measured at the IRGA on the flux tower.

$$Flux\ (wpl) = Flux\ (IRGA) + Flux\ (Latent\ Heat) + Flux\ (Sensible\ Heat) \qquad \textbf{6.iii}$$

Where the contribution to the total flux from Latent heat is equal to:-

$$Flux(Latent\ Heat) = (\mu wpl)\frac{(mean CO_2)}{(mean\ dry\ air\ density)}(Covariance\ Uz\ and\ H_2O)$$

6.iv

Where μwpl is a constant 29/18 which is the ratio of the molecular weight of dry air to that of water vapour, mean CO_2 (mg m^{-3}) is the average concentration of CO_2 measured at 4.5m at the top of the flux tower within a 30 minute sampling period. Mean air density (g m^{-3}) is the average dry air density measured at the top of the flux tower within a 30 minute sampling period. The covariance of Uz and H_2O is:-

$$Covariance\ (Uz, H_2O) = \frac{\sum\left((Uz - \overline{Uz})(H_2O - \overline{H_2O})\right)}{n} \qquad \textbf{6.v}$$

Where Uz is vertical wind speed (ms^{-1}) and H_2O is the density of water vapour measured at the flux tower (g m^{-3}). n is the number if measurements made of Uz and H_2O. The overbar denotes the mean value of the samples within a 30 minute sampling period.

Mean dry air density is equal to:-

$$Mean\ dry\ air\ density = \frac{(Mean\ Pressure)\ (mean\ vapour\ pressure)}{(mean\ temp)+273.15 \times RD} \qquad \textbf{6.vi}$$

Where the contribution to the total flux from sensible heat is:-

$$Flux(Sensible\ Heat) = (1+((\mu wpl)(\sigma wpl)))\left(\frac{(Mean\ CO_2)}{((Mean\ Temp)+273.15)}\right)\left(\frac{(Hcalc)}{(Mean\ air\ density)}\right)CP$$

6.vii

Where CP is a constant (1004.67) and is an estimate of the heat capacity of air (J $Kg^{-1}K^{-1}$). Where mean air density equals:-

$$mean\ air\ density = \frac{(mean\ dry\ air\ density\ +\ mean\ vapour\ denisty)}{1000} \qquad \textbf{6.viii}$$

Where mean vapour density equals:-

$$mean\ vapour\ density = \frac{mean\ vapour\ pressure}{(mean\ temp\ +\ 273.15) \times RV} \qquad \textbf{6.ix}$$

Where RV is the gas constant for water vapour ($Jmg^{-1}K^{-1}$) which equals R/18 and R ($8.3143x10^{-3}$ J K^{-1} $kmol^{-1}$) which is the universal gas constant.

Hcalc is equal to:-

$$Hcalc = \left(Hs\left(Mean\ air\ density \times CP \times 0.51 \times RD(Mean\ temp+273.15)^2\left(\frac{LEwpl}{(Mean\ Pressure \times LV)}\right)\right)\right) \times \left(\frac{(Mean\ Temp+273.15)}{(Mean\ Sonic\ Temp)+273.15}\right)$$

6.x

Where RD is the gas constant for dry air (R/29). LV is an estimate of the latent heat of vaporisation (2440 Jg^{-1}). Hs is equal to:-

$$Hs = (mean\ air\ density) \times CP \times (Covariance\ of\ Uz\ and\ Ts) \quad \textbf{6.xi}$$

LEwpl is equal to:-

$$LEwpl = (LEirga) + (H_2O\ wpl\ LE) + (H_2O\ wpl\ H) \quad \textbf{6.xii}$$

Where LEirga equals:-

$$LEirga = LV \times (Covariance\ of\ Uz\ and\ H_2O) \quad \textbf{6.xiii}$$

Where H_2O wpl LE equals:-

$$H_2O\ wpl\ LE = (\mu wpl) \times (\sigma wpl) \times (LEirga) \quad \textbf{6.xiv}$$

Where H_2O wpl H equals:-

$$H_2OwplH = 1 + ((\mu wpl)(\sigma wpl))\left(\frac{(Mean\ Vapour\ Density)}{(Mean\ Temp + 273.15)}\right) LV(Covariance\ Uz\ and\ Ts) \quad \textbf{6.xv}$$

Where Ts is sonic temperature

These are the basic equations which provide the flux measurements of the fluxes of carbon from a field site. These equations can be used over any time period, the time period used here is 30 minutes. These equations assume that the sensor is measuring carbon fluxes over a homogenous flat site, when in reality most sites are not homogenous. This leads on to the concept of the footprint. A footprint is used to describe the source area of turbulent scalar flux (Korman *et al.,* 2000). The footprint of a turbulent flux measurement defines the spatial context of the measurement, and due to the

inhomogeneous nature of most surfaces, the measured signal depends on which part of the surface has the strongest influence on the sensor, and thus on the location and size of the footprint (Schmid 2002).

The introductory equations for the footprint come from Korman *et al.*, (2000), and describe the equations needed to calculate the cumulative footprint for an upwind area of a flux tower, measuring the CO_2 flux via an eddy covariance method. The vertical turbulent flux $F(0,0,z_m)$ measured at a certain height (z_m) above the origin of the coordinate system (The location of the flux tower, with the certain height being the instrument height z_m at location 0,0,0), is related to the surface flux F(x,y,0) upwind of the measurement point by:-

$$F(0,0,z_m) = \int_{-\infty}^{\infty}\int_{0}^{\infty} F(x,y,0)\, \Phi(x,y,z_m)\, dx\, dy$$

6.xvi

Which is the same as equation 6.i defined by Schmid (2002). Where x,y,z_m are all coordinates of each measurement, where the flux measured at the flux tower is at coordinate $(0,0,z_m)$ and the location of the surface flux is (x,y,0). Where Φ = flux footprint, which describes the flux value, at location $(0,0,z_m)$, which is caused by a unit point source producing CO_2 at coordinate (x,y,0). This leads to the concept of a plume, where the unit point source producing CO_2 at the surface will release the CO_2 into the atmosphere, which will then disperse the CO_2 released depending on wind speed, direction, and concentration of ambient CO_2 towards the flux tower, which is different from the Schmid (2002) equation because air temperature is not implicitly implied by the initial equation. Therefore the concentration of CO_2 downwind of the unit point source at

the flux tower instrument height (z_m) can be described by the following equation:-

$$\gamma(x,y,z_m) = \frac{D_y(x,y)D_z(x,z)}{\bar{u}(x)} \qquad \textbf{6.xvii}$$

Where $Y(x,y,z_m)$ describes the concentration distribution of a unit point source at the instrument height. Where $D_y(x,y)$ = amount of dispersion of the plume by crosswind dispersion. This function will be based on the strength of the y wind speed crossing the x axis. It is assumed that crosswind dispersion is height independent. Where $D_z(x,z)$ = dispersion of the plume due to vertical dispersion. Where $\bar{u}(x)$ is the average plume velocity in the x direction. The flux footprint (Φ) can be defined by the equation:-

$$\Phi(x,y,z_m) = -K(z)\frac{\partial\gamma}{\partial z} = -K\frac{D_y}{\bar{u}}\frac{\partial D_z}{\partial z} \qquad \textbf{6.xviii}$$

Where K(z) = eddy diffusivity profile, which is a diffusing term for CO_2 over the distance between the unit point source and the flux tower. Integrating this equation (1.xvii) over the crosswind direction (y) becomes:-

$$f(x,z_m) = -\frac{K}{\bar{u}}\frac{\partial D_z}{\partial z} = -K\frac{\partial c(x,z)}{\partial z} \qquad \textbf{6.xix}$$

Where $f(x,z_m)$ is the crosswind integrated flux footprint or vertical flux per unit, and differs from $\Phi(x,y,z_m)$ which is the flux footprint or vertical flux per unit point source. C(x,z) is the crosswind integrated concentration per unit point source, and is defined as:-

$$c(x,z) = \frac{D_z}{\bar{u}}\int_{\infty}^{\infty}\gamma dy \quad and \quad f(x,z) = \int_{-\infty}^{\infty}\varphi dy \qquad \textbf{6.xx}$$

The crosswind distributed concentration (Y) and footprint (Φ) are therefore related to the

crosswind integrated quantities via:-

$$\gamma = D_y c \quad \text{and} \quad \Phi = Dyf \qquad \textbf{6.xxi}$$

It is assumed that there is a normal or Gaussian crosswind distribution function:-

$$D_y(x,y) = \frac{1}{\sqrt{2\Pi}\sigma}\exp\left(\frac{y^2}{2\sigma^2}\right) \qquad \textbf{6.xxii}$$

Where $\sigma = \sigma_y\,(x)$

$\sigma = c_1 x\,(1+c_2 x)$ where $c_1 = 0.32$, and $c_2 = 0.0004$

$\sigma = \sigma_v x / \bar{u}$ where σ_v = crosswind constant fluctuation

Finally, the stationary diffusion problem is described completely by introducing the continuity equation, which reduces to a two dimensional advection – diffusion equation:-

$$u = \frac{\partial c}{\partial x} = \frac{\partial f}{\partial z} \qquad \textbf{6.xxiii}$$

This equation neglects horizontal turbulent diffusion along the streamlines compared to advection, in addition to the already mentioned simplications of height-independent crosswind dispersion and first-order closure or gradient diffusion. This leads to the defining of the analytical footprint model again based on Kormann *et al.*, (2001). It is assumed that there is a power law relationship between the vertical profile of the horizontal wind velocity (u(z)) and eddy diffusivity (K(z)):-

$$u(z) = U z^m \quad \text{and} \quad K(z) = kz^n \qquad \textbf{6.xxiv}$$

Where U is a constant in power law profile of the wind velocity, and k is a constant in power law profile of the eddy diffusivity, and m and n are related to the shape function r,

defined later. If there is a power law relationship then this will lead to the following equation:-

$$c(x,z) = \frac{A}{\bar{z}\,\bar{u}} \exp\left[\left(\frac{Bz}{\bar{z}}\right)^{r} \right] \qquad \textbf{6.xxv}$$

Where, A, and B are constants defined below, $z \equiv$ average plume height. r = 2+m-n.

$$A = \frac{r\Gamma(2/r)}{\Gamma(1/r)^2} \quad \text{and} \quad B = \frac{\Gamma(2/r)}{\Gamma(1/r)} \qquad \textbf{6.xxvi}$$

Where Γ is the gamma function.

The dependence on downwind distance (x) is expressed through the average plume height:-

$$\bar{z}(x) = \int_0^\infty zc\,dz / \int_0^\infty c\,dz \qquad \textbf{6.xxvii}$$

The effective plume velocity ($\bar{u}$) is:-

$$\bar{u}(x) = \int_0^\infty uc\,dz / \int_0^\infty c\,dz \qquad \textbf{6.xxviii}$$

The differential equation of equation 6.xxvii for the mean height is:-

$$\frac{d\bar{z}}{dx} = rB^r \frac{k}{U} z^{-1-r} \qquad \textbf{6.xxix}$$

Integrating this equation gives:-

$$\bar{z}(x) = B\left(\frac{r^2 k}{U}\right)^{1/r} x^{1/r} \qquad \textbf{6.xxx}$$

It is deduced, with equations, 6.xxvii, 6.xxxi, and 6.xxxii, that:-

$$\overline{u}(x) = \frac{\Gamma(\mu)}{\Gamma(1/r)}\left(\frac{r^2 k}{U}\right)^{m/r} U x^{m/r} \qquad \textbf{6.xxxi}$$

Where $\mu = (1+m)/r$. Defining a length term as:-

$$\xi(z) = \frac{U z^r}{r^2 k} \qquad \textbf{6.xxxii}$$

Equation6.xxv can be written as:-

$$c = \frac{1}{\Gamma(\mu)} \frac{r}{U z^{1+m}} \frac{\xi^{\mu}}{x^{\mu}} \exp^{\xi\xi/} \qquad \textbf{6.xxxiii}$$

Relating these equations to the crosswind integrated flux footprint gives:-

$$f = \frac{1}{\Gamma(\mu)} \frac{\xi^{\mu}}{x^{1+\mu}} \exp^{\xi\xi/} \qquad \textbf{6.xxxiv}$$

Kormann states that this is a coordinate transformation that is not explicitly included formulae. Combining equations 6.xxxii and 6.xxiii, solves equation 6.xxi and 6.xxii. Footprint measurements are dependent upon the sensor height, the wind speed, the friction velocity, often called U*, the stability of the air, and is defined as a parameter with dimension of length that gives a relation between parameters characterizing dynamic, thermal, and buoyant processes, and is called the Obukhov length:-

$$L = \frac{-u_*^3 \, T_v}{\kappa g Q_{vo}} \qquad \textbf{6.xxxv}$$

Where k = von Kármán's constant (= 0.4 ±0.01), U_* = friction velocity, which is a

measure of turbulent velocity, g = gravitational acceleration, T_v = virtual temperature, and Q_{vo} = kinematic virtual temperature flux at the surface (American Meteorological Society Glossary of Meteorology website). An instantaneous footprint can only give a concentration gradient away from the flux tower in the instantaneous wind direction. Therefore a much better expression of concentration sources of a sampling area is an averaged footprint which will show the areas that are normally high, or release CO_2 and there location and the areas that are sinks of carbon for a sampling area, and how much carbon on average the sampling area will take up.

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